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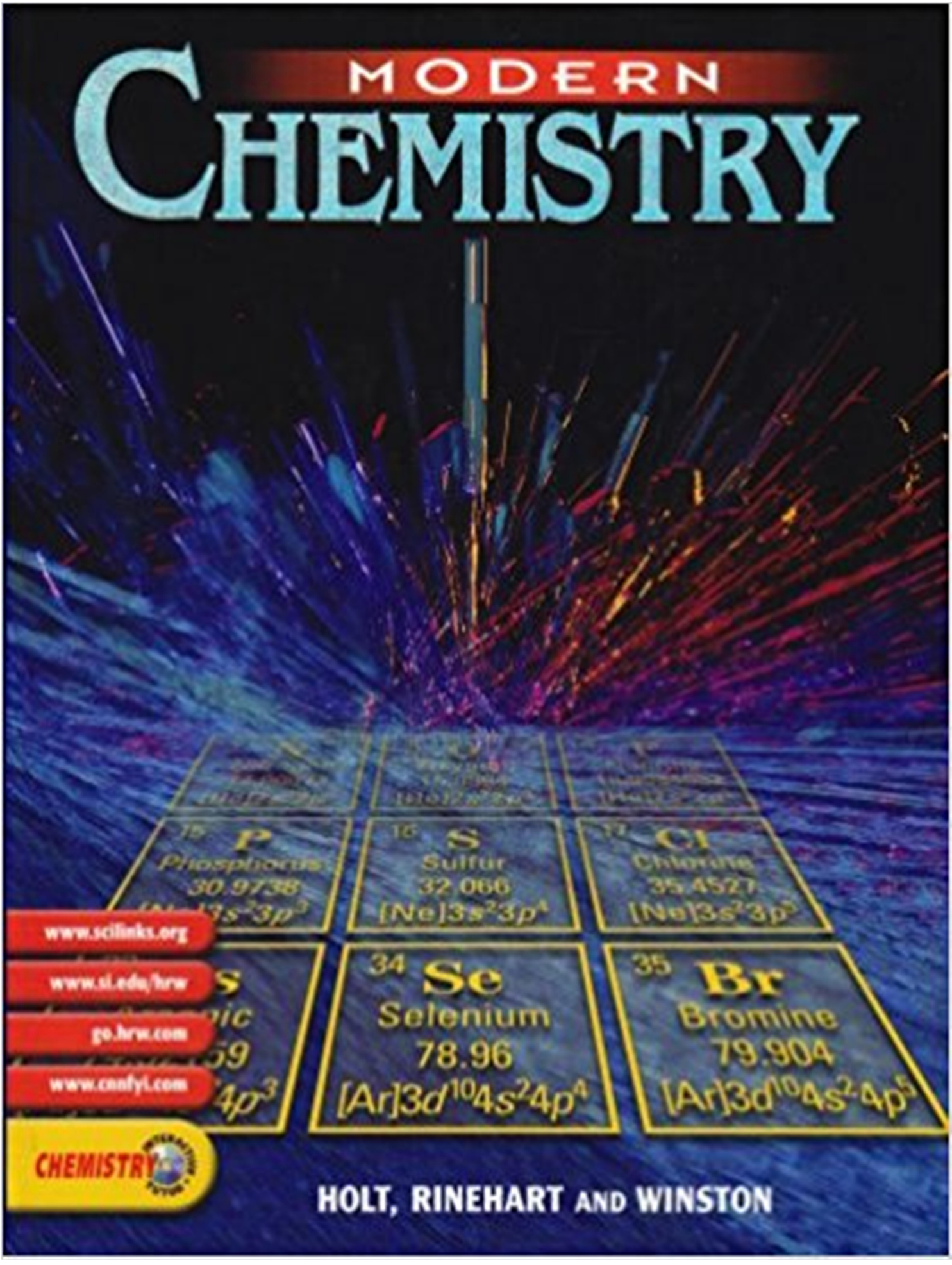

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Cover: Portion of the periodic table superimposed on a photomicrograph of crystals of the amino-acid dimer cystine. Photo by © Mel Pollinger/Fran Heyl Associates, NY

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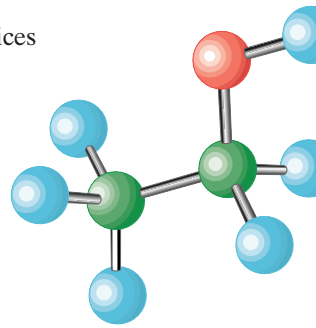

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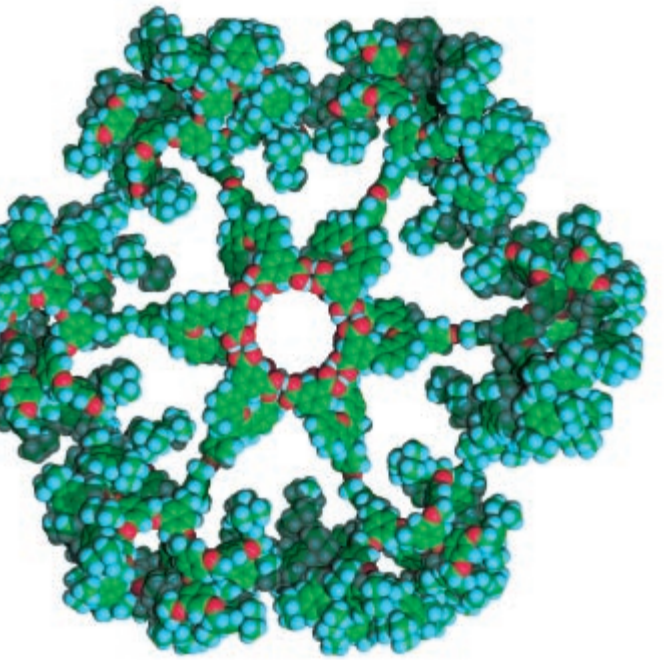

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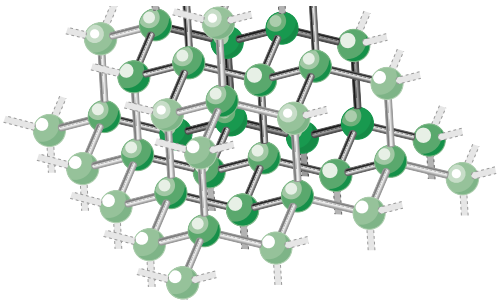

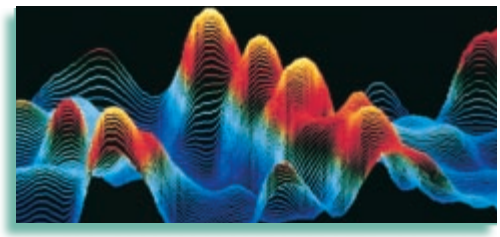

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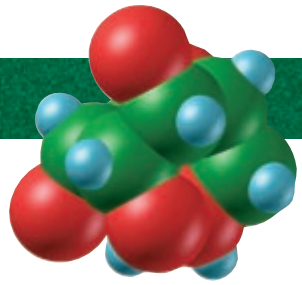

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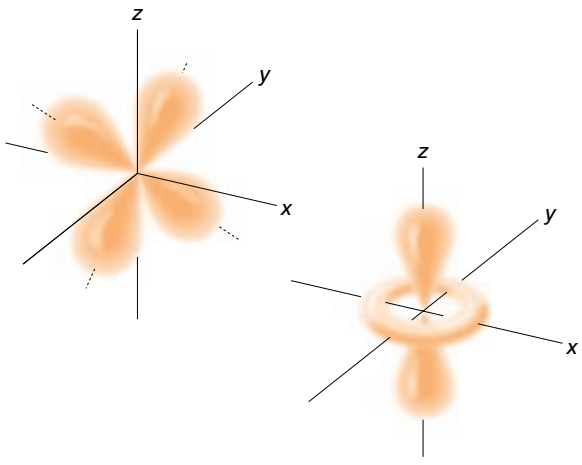

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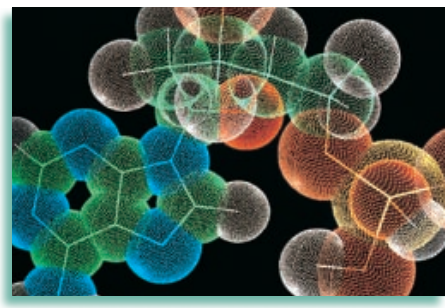

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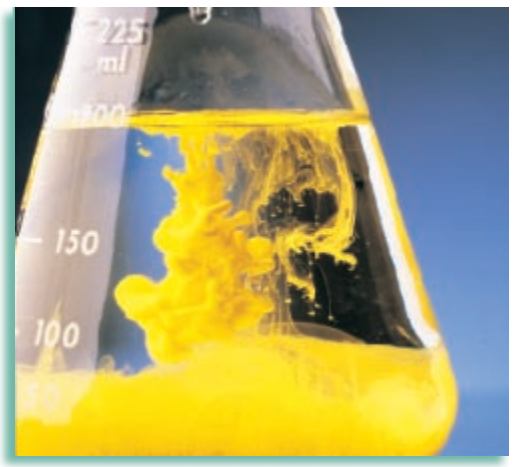

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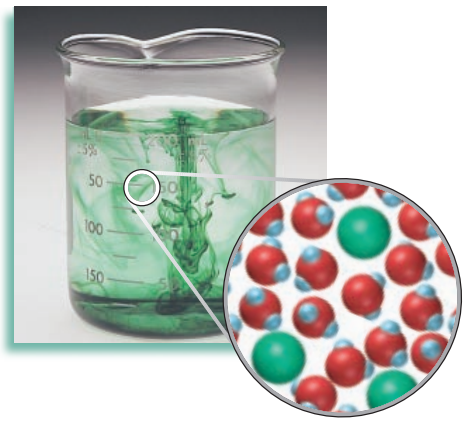

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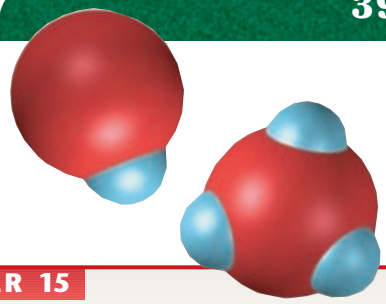

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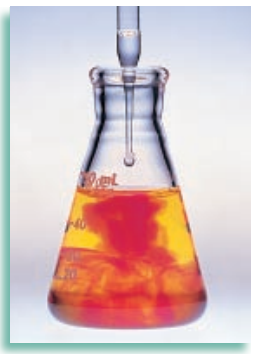

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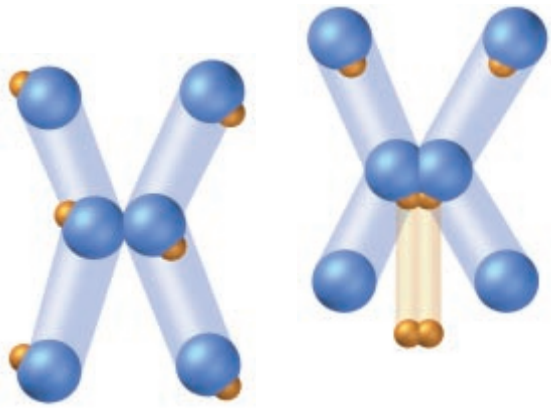

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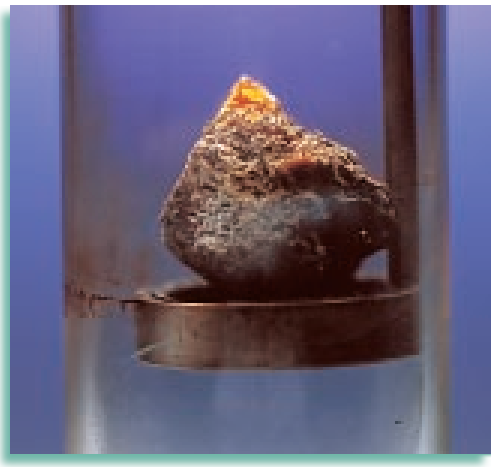

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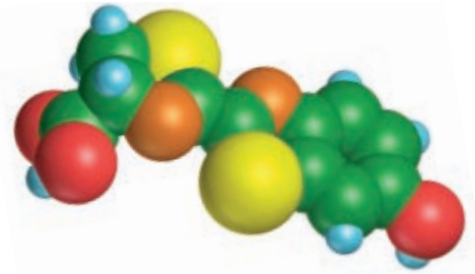

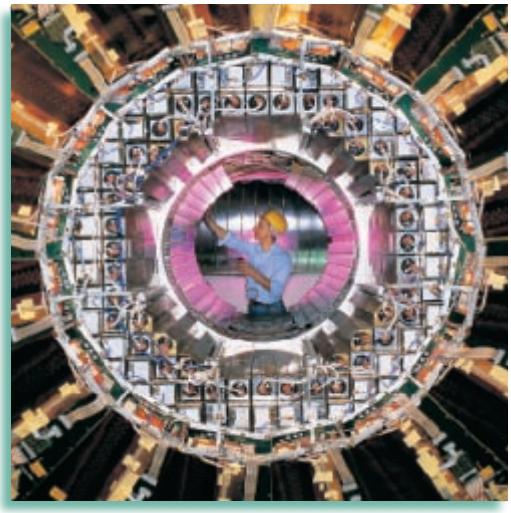

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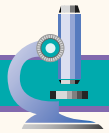

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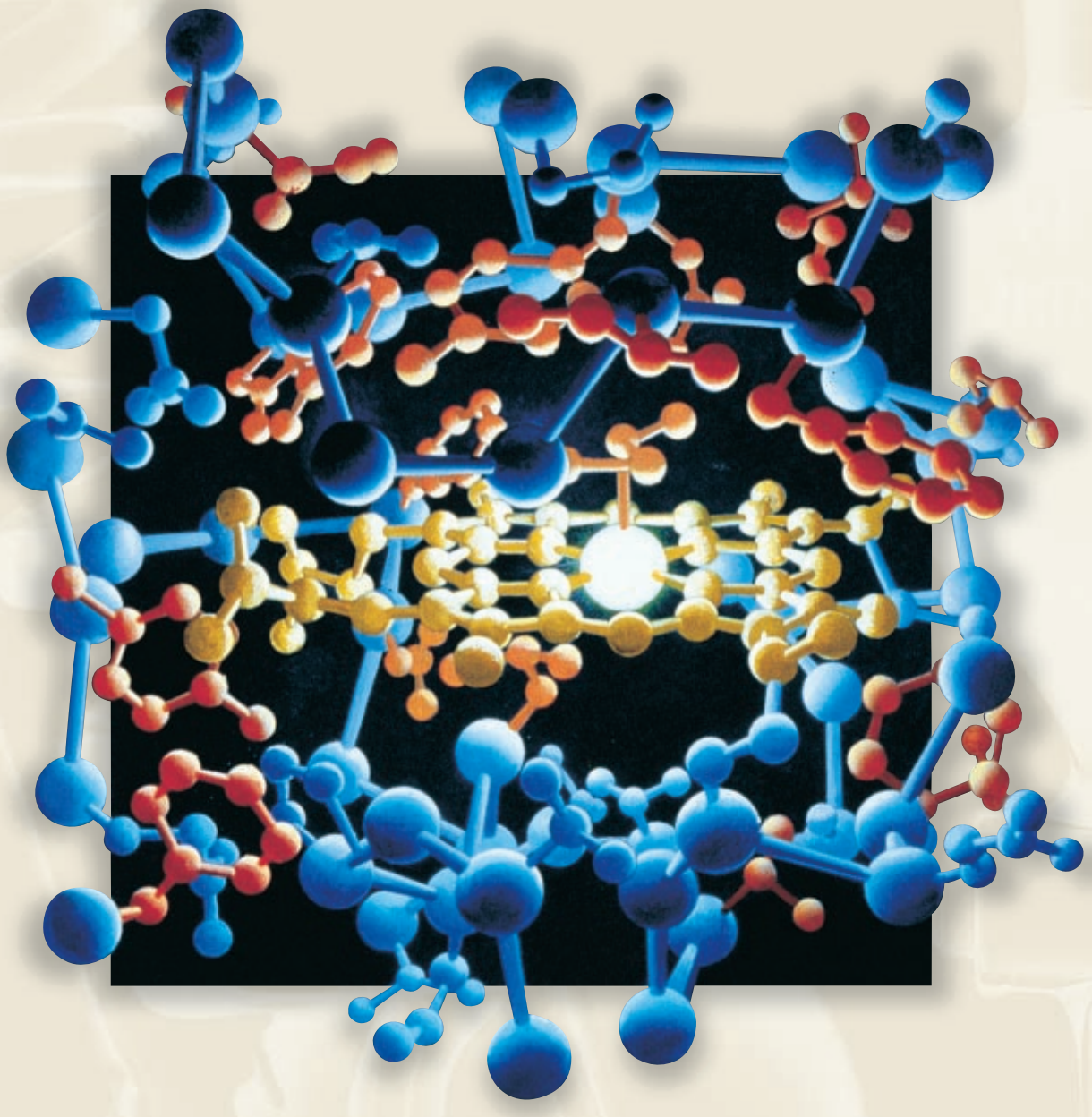
CHAPTER 1

Matter and Change



Chemistry is central to all of the sciences.

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Chemistry Is a Physical Science

SECTION 1-1

Objectives

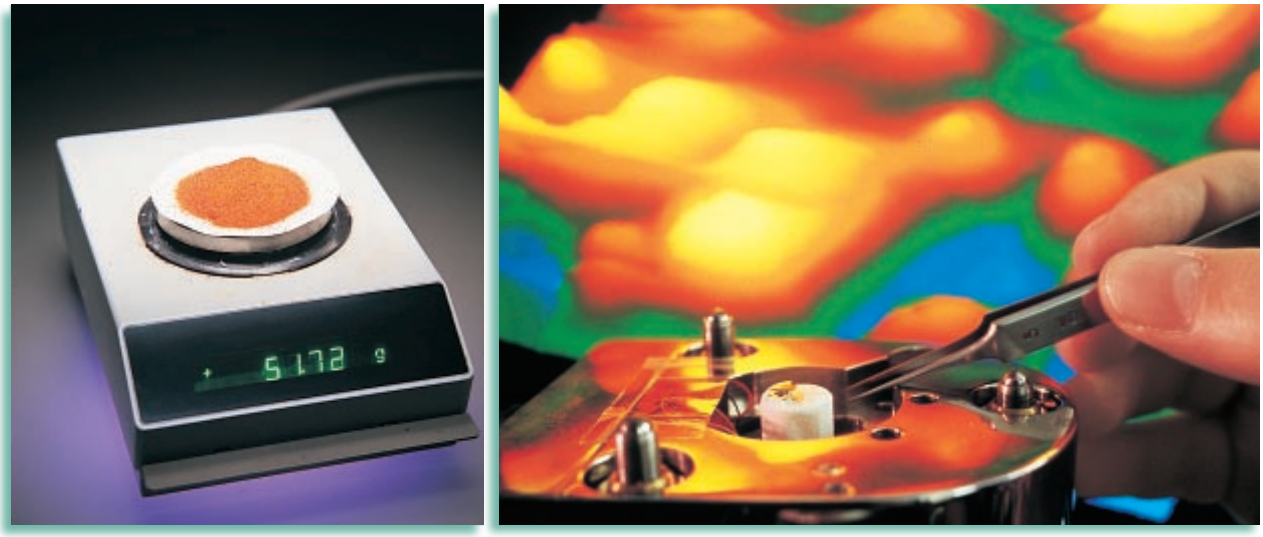
- Define *chemistry*.
- List examples of the branches of chemistry.
- Compare and contrast basic research, applied research, and technological development.

The natural sciences were once divided into two broad categories: the biological sciences and the physical sciences. Living things are the main focus of the biological sciences. The physical sciences focus mainly on nonliving things. However, because we now know that both living and nonliving matter have a chemical structure, chemistry is central to all the sciences, and there are no longer distinct divisions between the biological and physical sciences.

Chemistry *is the study of the composition, structure, and properties of matter and the changes it undergoes*. Chemistry deals with questions such as, What is that material made of? What is its makeup and internal arrangement? How does it behave and change when heated, cooled, or mixed with other materials and why does this behavior occur? Chemists answer these kinds of questions in their daily work.

Instruments are routinely used in chemistry to extend our ability to observe and make measurements. Instruments make it possible, for example, to look at microstructures—things too tiny to be seen with the unaided eye. The scanning electron microscope reveals tiny structures by beaming particles called electrons at materials. When the electrons hit a material, they scatter and produce a pattern that shows the material's microstructure. Invisible rays called X rays can also be used to

FIGURE 1-1 A balance (a) is an instrument used to measure the mass of materials. A sample of DNA placed in a scanning tunneling microscope produces an image (b) showing the contours of the DNA's surface.



(a) (b)

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"look at" microstructures. The patterns that appear, called X-ray diffraction patterns, can be analyzed to reveal the arrangement of atoms, molecules, or other particles that make up the material. By learning about microstructures, chemists can explain the behavior of macrostructures—the visible things all around you.

Branches of Chemistry

Chemistry includes many different branches of study and research. The following are six main areas, or branches, of study. But like the biological and physical sciences, these branches often overlap.

1. *Organic chemistry*—the study of most carbon-containing compounds
2. *Inorganic chemistry*—the study of all substances not classified as organic, mainly those compounds that do not contain carbon
3. *Physical chemistry*—the study of the properties and changes of matter and their relation to energy
4. *Analytical chemistry*—the identification of the components and composition of materials
5. *Biochemistry*—the study of substances and processes occurring in living things
6. *Theoretical chemistry*—the use of mathematics and computers to understand the principles behind observed chemical behavior and to design and predict the properties of new compounds

In all areas of chemistry, scientists work with chemicals. *A* **chemical** *is any substance that has a definite composition.* For example, consider the material called sucrose, or cane sugar. It has a definite composition in terms of the atoms that compose it. It is produced by certain plants in the chemical process of photosynthesis. Sucrose is a chemical. Carbon dioxide, water, and countless other substances are chemicals as well.

Knowing the properties of chemicals allows chemists to find suitable uses for them. For example, researchers have synthesized new substances, such as artificial sweeteners and synthetic fibers. The reactions used to make these chemicals are carried out on a large scale to make new products such as sweeteners and fabrics available for consumers.

Basic Research

Basic research is carried out for the sake of increasing knowledge, such as how and why a specific reaction occurs and what the properties of a substance are. Chance discoveries can be the result of basic research. The properties of Teflon, for example, were first discovered by accident. A researcher named Roy Plunkett was puzzled by the fact that a gas cylinder used for an experiment appeared to be empty even though the measured mass of the cylinder clearly indicated there was something inside. Plunkett cut the cylinder open and found a white solid. Through basic research, Plunkett's research team determined the nonstick properties, chemical structure, and chemical composition of the new material.

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Applied Research

Applied research is generally carried out to solve a problem. For example, when refrigerants escape into the upper atmosphere, they damage the ozone layer, which helps block harmful ultraviolet rays from reaching the surface of Earth. In response to concerns that this atmospheric damage could pose potential health problems, chemists have developed new refrigerants. In applied research, the researchers are driven not by simple curiosity or a desire to know but by a desire to solve a specific problem.

Technological Development

Technological development typically involves the production and use of products that improve our quality of life. Examples include computers, catalytic converters for cars, and biodegradable materials.

FIGURE 1-2 The chemical structure of the material in an optical fiber gives it the property of total internal reflection. This property, which allows these fibers to carry light, was discovered through basic and applied research. The use of this property to build telecommunications networks by sending data on light pulses is the technological development of fiber optics.

Technological applications often lag far behind the basic discoveries that are eventually used in the technologies. For example, nonstick cookware, a technological application, was developed well after the accidental discovery of Teflon. When it was later discovered that the Teflon coating on cookware often peeled off, a new problem had to be solved. Using applied research, scientists were then able to improve the bond between the Teflon and the metal surface of the cookware so that it did not peel.

Basic research, applied research, and technological development often overlap. Discoveries made in basic research may trigger ideas for applications that can result in new technologies. For example, knowledge of crystals and the behavior of light was gained from basic research, and this knowledge was used to develop lasers. It was then discovered that pulses of light from lasers can be sent through optical fibers. Today, information, such as telephone messages and cable television signals, can now be carried quickly over long distances using fiber optics.

SECTION REVIEW

1. Define *chemistry*.
2. Name the six branches of study in chemistry.
3. Compare and contrast basic research, applied research, and technological development.

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Modern Alchemy

HISTORICAL PERSPECTIVE

Until a hundred years ago, chemists were still debating the validity of John Dalton's atomic theory. Few, however, challenged the notion that the elements were unchangeable. Near the beginning of the twentieth century, the discovery of some new elements and the strange radiation they emitted established the connection between atoms and the elements while resurrecting an ancient notion long discarded by science.

Before Chemistry

Until the chemical revolution of the seventeenth and eighteenth centuries, most theories about matter were based on the ideas of the ancient Greek philosopher Aristotle. He postulated that all matter consisted of four elements: earth, water, air, and fire. In turn, each of these elements exhibited two of four fundamental properties: moistness, dryness, coldness, and hotness. By altering these basic properties, Aristotle claimed, the elements could be transformed, or transmuted, into one another.

The interior of an alchemist's laboratory is depicted by artist Eugene Isabey.

The practical pursuit of transmutation became known as alchemy, and for more than 1,500 years investigators searched in vain for alchemical methods that would transform common metals such as mercury and lead into precious gold. Then, in the seventeenth century, chemists began to question Aristotle's assumptions. They defined an element as a material that can't be broken down into simpler substances, and with no evidence to support the possibility of transmutation of the modern elements, alchemy fell into ill repute.

Strange Rays

In 1896, French scientist Henri Becquerel discovered that the element uranium gave off a strange, invisible radiation. The report of these "uranic rays" caught the attention of a young chemist by the name of Marie Curie.

Working with her husband, Pierre, Marie began to test various substances for radioactivity. Analyzing a mineral composite called pitchblende, a known source of uranium, she was startled to find that the composite's level of radioactivity was greater than that of a similar amount of pure uranium. This meant that another radioactive material besides uranium was present in the pitchblende.

After months of tedious work, Marie had isolated two new radioactive elements, which she

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named polonium and radium, from pitchblende. Curie later won the Nobel Prize for her discovery, but at the time, she was troubled by the seemingly constant energy source of the radioactive process that had led her to the new elements. As she wrote in 1900:

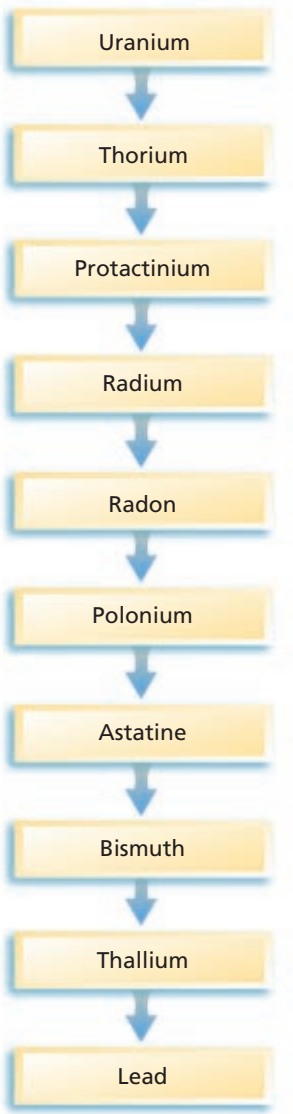
> *The emission of the uranic rays is very constant . . . The uranium shows no appreciable change of state, no visible chemical transformation, it remains, in appearance at least, the same as ever, the source of the energy it discharges remains undetectable. . . .*

The Revival of Transmutation

While Marie Curie was making her momentous discoveries, other scientists were establishing that the chemical elements were actually different types of atoms. The connection between this emerging theory of matter and radioactivity was made by the famous scientist Ernest Rutherford.

In 1902, Rutherford and his assistant, Frederick Soddy, reported that the radioactivity of a sealed sample of thorium (a known element determined to be radioactive by the Curies) had actually *increased* over time. This increase was accompanied by the simultaneous evolution of a radioactive gas. The two investigators began to question whether radioactive elements were as stable as elements were supposed to be. After further studies, Rutherford and Soddy presented their shocking explanation:

> *The cause and nature of radioactivity is at once an atomic phenomenon and the accompaniment of a chemical change in which new kinds of matter are produced. The two considerations force us to the conclusion that radioactivity is a manifestation of subatomic chemical change.*



A simplified decay diagram for uranium

Rutherford and Soddy's "subatomic chemical change" was nothing less than transmutation. Nature had turned out to be an alchemist!

The New Alchemy Explained

Rutherford later showed that the spontaneous transmutation, or decay, of radioactive atoms involves the emission of nuclear particles or high-energy waves known as gamma rays, or both. The atom's nucleus is consequently reconfigured, changing the atom into that of another element.

Thus, the source of energy in Marie Curie's uranium sample came from within the radioactive atoms. And although it seemed as if the energy output was constant, the sources of the radiation were continually changing as one radioactive element decayed into another.

Years later, it would be shown that the transmutation of certain elements could be deliberately initiated by bombarding nuclei with accelerated subatomic particles. But the goal of modern alchemy is no longer gold, as Soddy remarked in 1917:

> *If man ever achieves this control over Nature, it is quite certain that the last thing he would want to do would be to turn lead or mercury into gold*—for the sake of gold. *The energy that would be liberated, if the control of these sub-atomic processes were possible . . . would far exceed in importance and value the gold.*

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SECTION 1-2

Matter and Its Properties

Objectives

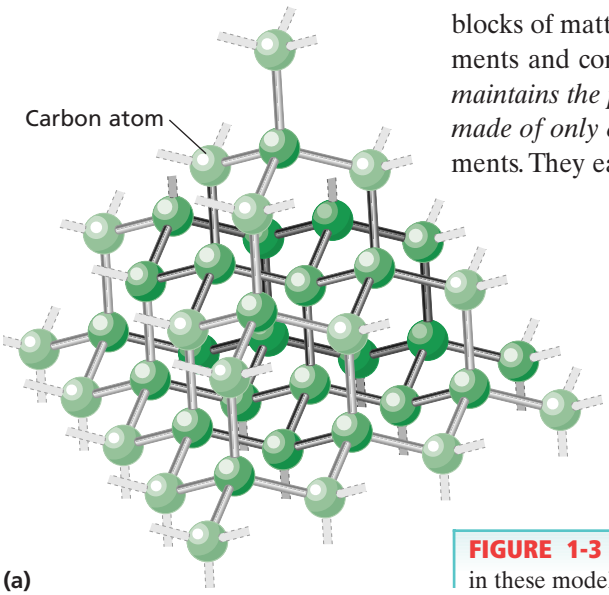
- Distinguish between the physical properties and chemical properties of matter.
- Classify changes of matter as physical or chemical.
- Explain the gas, liquid, and solid states in terms of particles.
- Distinguish between a mixture and a pure substance.

Look around you. You can see a variety of objects—books, desks, chairs, and perhaps trees or buildings outside. All those things are made up of matter, but exactly what is matter? What characteristics, or properties, make matter what it is? In this section, you will learn the answers to these questions.

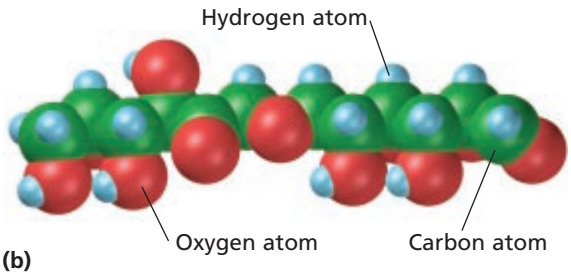
Explaining what matter is involves finding properties that all matter has in common. That may seem difficult, given that matter takes so many different forms. For the moment, just consider one example of matter—a rock. The first thing you might notice is that the rock takes up space. In other words, it has *volume*. Volume is the amount of three-dimensional space an object occupies. All matter has volume. All matter also has a property called mass. **Mass** *is a measure of the amount of matter*. Mass is the measurement you make using a balance. **Matter** can thus be defined as *anything that has mass and takes up space*. These two properties are the general properties of all matter.

Basic Building Blocks of Matter

You know that matter comes in many forms. The fundamental building blocks of matter are atoms and molecules. These particles make up elements and compounds. *An* **atom** *is the smallest unit of an element that maintains the properties of that element. An* **element** *is a pure substance made of only one kind of atom.* Carbon, hydrogen, and oxygen are elements. They each contain only one kind of atom.



(a)



(b)

FIGURE 1-3 Both elements and compounds are made of atoms, as shown in these models of (a) diamond and (b) sucrose (table sugar).

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A **compound** *is a substance that is made from the atoms of two or more elements that are chemically bonded.* Many compounds consist of molecules. Water is an example of a compound. It is made of two elements, hydrogen and oxygen. The atoms of hydrogen and oxygen are chemically bonded to form a water molecule. You will learn more about the particles that make up compounds when you study chemical bonding in Chapter 6. For now, you can think of a *molecule* as the smallest unit of an element or compound that retains all of the properties of that element or compound.

Properties and Changes in Matter

Every substance, whether it is an element or a compound, has characteristic properties. Chemists use properties to distinguish between substances and to separate them. Most chemical investigations are related to or depend on the properties of substances.

A property may be a characteristic that defines an entire group of substances. That property can be used to classify an unknown substance as a member of that group. For example, one large group of elements is the metals. The distinguishing property of metals is that they conduct electricity well. Therefore, if an unknown element is tested and found to conduct electricity well, it is a metal.

Properties can help reveal the identity of an unknown substance. However, conclusive identification usually cannot be made based on only one property. Comparisons of several properties can be used together to establish the identity of an unknown. Properties are either intensive or extensive. **Extensive properties** *depend on the amount of matter that is present.* Such properties include volume, mass, and the amount of energy in a substance. In contrast, **intensive properties** *do not depend on the amount of matter present.* Such properties include the melting point, boiling point, density, and ability to conduct electricity and heat. These properties are the same for a given substance regardless of how much of the substance is present. Properties can also be grouped into two general types: physical properties and chemical properties.

FIGURE 1-4 Because it possesses certain chemical properties, a test strip containing Benedict's solution is used to test for the presence of sugar in urine. The test strip is dipped into the sample. The test strip is then matched to a color scale to determine the sugar level in the urine.

Physical Properties and Physical Changes

A **physical property** *is a characteristic that can be observed or measured without changing the identity of the substance.* Physical properties describe the substance itself, rather than describing how it can change into other substances. Examples of physical properties are melting point and boiling point. Those points are, respectively, the temperature at which a substance melts from solid to liquid and the temperature at which it boils from liquid to gas. For example, water melts from ice to liquid at 0°C (273 K or 32°F). Liquid water boils to vapor at 100°C (373 K or 212°F).

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A change in a substance that does not involve a change in the identity of the substance is called a **physical change.** Examples of physical changes include grinding, cutting, melting, and boiling a material. These types of changes do not change the identity of the substance present.

Melting and boiling are part of an important class of physical changes called changes of state. As the name suggests, *a* **change of state** *is a physical change of a substance from one state to another.* The three common states of matter are solid, liquid, and gas.

Matter in the **solid** *state has definite volume and definite shape.* For example, a piece of quartz or coal keeps its size and its shape, regardless of the container it is in. Solids have this characteristic because the particles in them are packed together in relatively fixed positions. The particles are held close together by strong attractive forces between them, and only vibrate about fixed points.

Matter in the **liquid** *state has a definite volume but an indefinite shape;* a liquid assumes the shape of its container. For example, a given quantity of liquid water takes up a definite amount of space, but the water takes the shape of its container. Liquids have this characteristic because the particles in them are close together but can move past one another. The particles in a liquid move more rapidly than those in a solid. This causes them to overcome temporarily the attractive forces between them, allowing the liquid to flow.

Matter in the **gas** *state has neither definite volume nor definite shape.* For example, a given quantity of helium expands to fill any size container and takes the shape of the container. All gases have this characteristic because they are composed of particles that move very rapidly and are at great distances from one another compared with the particles of liquids and solids.

At these great distances, the attractive forces between gas particles are much weaker than those in liquids and solids.

An important fourth state of matter is **plasma.** Plasma is a *high-temperature physical state of matter in which atoms lose their electrons* (which you may know about from your earlier work in general science). Plasma is found in a fluorescent bulb.

Melting, the change from solid to liquid, is an example of a change of state. Boiling is a change of state from liquid to gas. Freezing, the opposite of melting, is the change from a liquid to a solid. A change of state does not affect the identity of the substance. For example, when ice melts to liquid water or when liquid water boils to form water vapor, the same substance, water, is still present, as shown in Figure 1-6. The water has simply changed state, but it has not turned into a different compound. Only the distances and interactions between the particles that make up water have changed.

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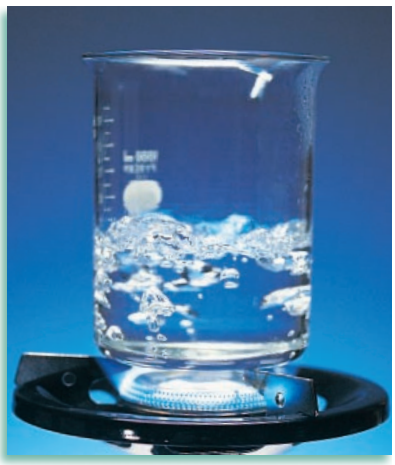

FIGURE 1-5 Water boils at 100°C no matter how much water is in the container. Boiling point is an intensive property.

Chemical Properties and Chemical Changes

Physical properties can be observed without changing the identity of the substance, but properties of the second type—chemical properties—cannot. *A* **chemical property** *relates to a substance's ability to undergo changes that transform it into different substances.* Chemical properties are easiest to see when substances react to form new substances.

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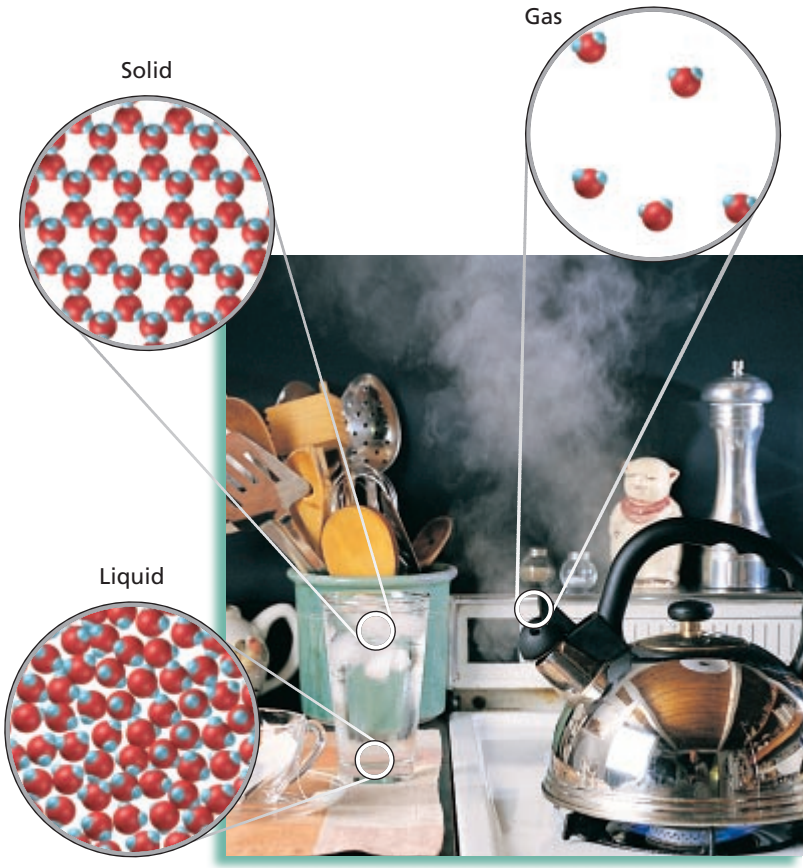

FIGURE 1-6 Models for water in three states. The molecules are close together in the solid and liquid states but far apart in the gas state. The molecules in the solid state are relatively fixed in position, but those in the liquid and gas states can flow around each other.

For example, the ability of charcoal (carbon) to burn in air is a chemical property. When charcoal burns, it combines with oxygen in air to become a new substance, carbon dioxide gas. After the chemical change, the original substances, carbon and oxygen, are no longer present. A different substance with different properties has been formed. Other examples of chemical properties include the ability of iron to rust by combining with oxygen in air and the ability of silver to tarnish by combining with sulfur.

A change in which one or more substances are converted into different substances is called a **chemical change** *or* **chemical reaction.** *The substances that react in a chemical change are called the* **reactants.** *The substances that are formed by the chemical change are called the* **products.** In the case of burning charcoal, carbon and oxygen are the reactants in a combustion, or burning, reaction. Carbon dioxide is the product. The chemical change can be described as follows:

Carbon plus oxygen yields (or forms) carbon dioxide.

Arrows and plus signs can be substituted for the words *yields* and *plus,* respectively:

$$\text{carbon} + \text{oxygen} \longrightarrow \text{carbon dioxide}$$

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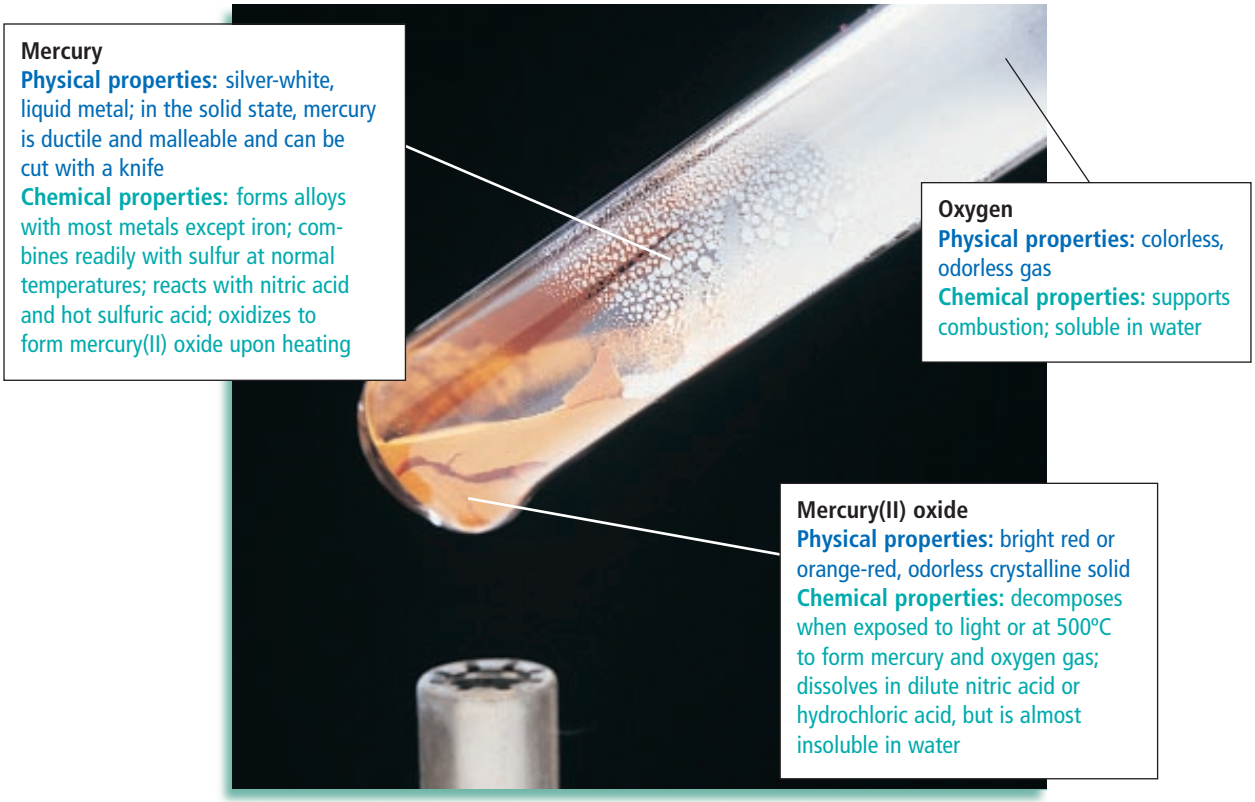
Mercury
Physical properties: silver-white, liquid metal; in the solid state, mercury is ductile and malleable and can be cut with a knife
Chemical properties: forms alloys with most metals except iron; combines readily with sulfur at normal temperatures; reacts with nitric acid and hot sulfuric acid; oxidizes to form mercury(II) oxide upon heating
Oxygen
Physical properties: colorless, odorless gas
Chemical properties: supports combustion; soluble in water
Mercury(II) oxide
Physical properties: bright red or orange-red, odorless crystalline solid
Chemical properties: decomposes when exposed to light or at 500°C to form mercury and oxygen gas; dissolves in dilute nitric acid or hydrochloric acid, but is almost insoluble in water

FIGURE 1-7 When mercury(II) oxide is heated, it decomposes to form oxygen gas and mercury (which can be seen on the side of the test tube). Decomposition is a chemical change that can be observed by comparing the properties of mercury(II) oxide, mercury, and oxygen.

The decomposition of the mercury compound shown in Figure 1-7 can be expressed as follows:

$$\text{mercury(II) oxide} \longrightarrow \text{mercury} + \text{oxygen}$$

Chemical changes and reactions, such as combustion and decomposition, form products whose properties differ greatly from those of the reactants. However, chemical changes do not affect the total amount of matter present before and after a reaction. The amount of matter, and therefore the total mass, remains the same.

Energy and Changes in Matter

When physical or chemical changes occur, energy is always involved. The energy can take several different forms, such as heat or light. Sometimes heat provides enough energy to cause a physical change, as in the melting of ice, and sometimes heat provides enough energy to cause a chemical change, as in the decomposition of water vapor to form oxygen gas and hydrogen gas. But the boundary between physical and chemical changes isn't always so clear. For example, while most chemists would consider the dissolving of sucrose in water to be a physical change, many chemists would consider the dissolving of table salt in water to be a chemical change. As you learn more about the structure of matter, you will better understand why the boundaries between chemical and physical changes can be confusing.

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Although energy can be absorbed or released in a change, it is not destroyed or created. It simply assumes a different form. This is the law of conservation of energy. Accounting for all the energy present before and after a change is not a simple process. But scientists who have done such experimentation are confident that the total amount of energy remains the same.

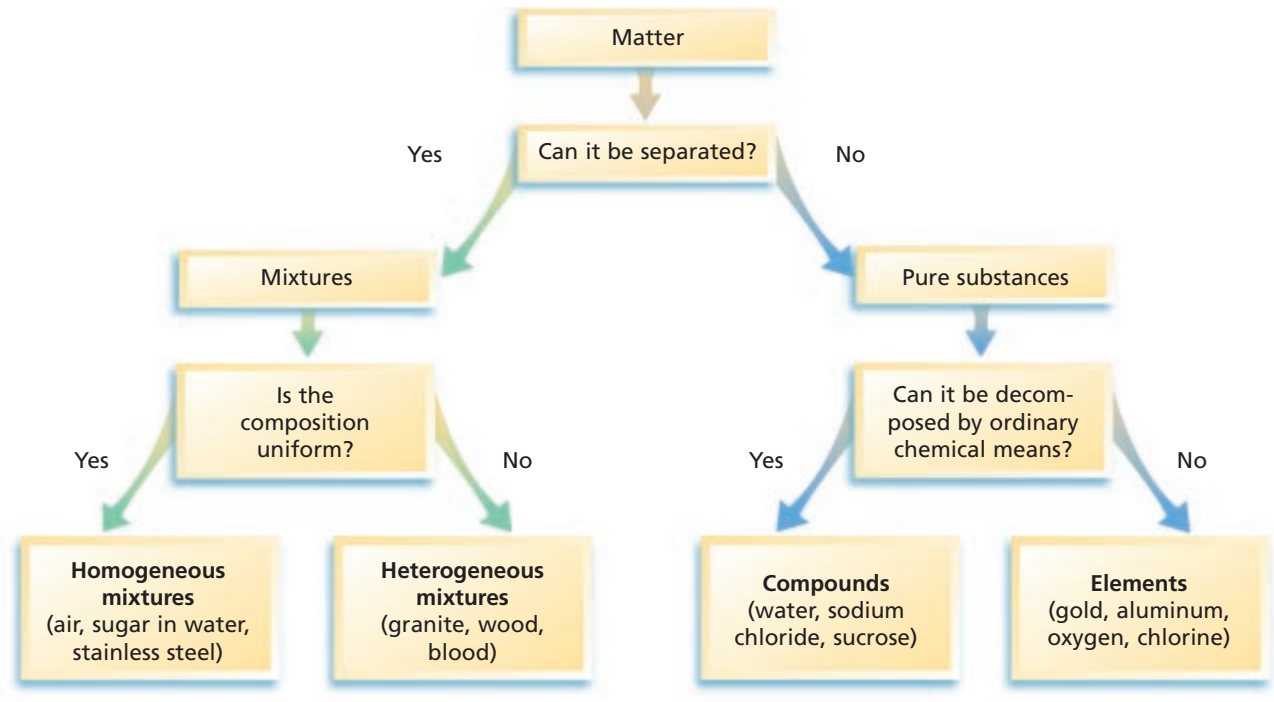
Classification of Matter

The variety of forms in which matter exists is enormous. However, all matter can be classified into one of two groups: pure substances or mixtures. A pure substance can be an element or compound. The composition of a pure substance is the same throughout and does not vary from sample to sample. Mixtures, in contrast, contain more than one substance. They can vary in composition and properties from sample to sample and sometimes from one part of a sample to another part of the same sample. All matter, whether it is a pure substance or a mixture, can be classified in terms of uniformity of composition and properties of a given sample. Figure 1-8 illustrates the overall classification of matter into elements, compounds, and mixtures.

Mixtures

You deal with mixtures every day. Nearly every object around you, including most things you eat and drink and even the air you breathe, is a mixture. *A* **mixture** *is a blend of two or more kinds of matter, each*

FIGURE 1-8 This classification scheme for matter shows the relationships among mixtures, compounds, and elements.



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(a)

(b)

(c)

FIGURE 1-9 (a) Barium chromate can be separated from the solution in the beaker using filtration. (b) A centrifuge can be used to separate certain solid components. The centrifuge spins rapidly, which causes the solids to settle to the bottom of the test tube. (c) The components of an ink can be separated using paper chromatography.

of which retains its own identity and properties. The parts, or components, of a mixture are simply mixed together physically and can usually be separated. As a result, the properties of a mixture are a combination of the properties of its components. Because mixtures can contain various amounts of different substances, a mixture's composition must be specified. This is often done in terms of percentage by mass or by volume. For example, a mixture might be 5% sodium chloride and 95% water by mass.

Some mixtures are *uniform in composition;* that is, they are said to be **homogeneous.** They have the same proportion of components throughout. *Homogeneous mixtures are also called* **solutions.** A salt-water solution is an example of such a mixture. Other mixtures are *not uniform throughout;* that is, they are **heterogeneous.** For example, in a mixture of clay and water, heavier clay particles concentrate near the bottom of the container.

Some mixtures can be separated by filtration or vaporized to separate the different components. Filtration can be used to separate a mixture of solid barium chromate from the other substances, as shown in the beaker in Figure 1-9(a). The yellow barium compound is trapped by the filter paper, but the solution passes through. If the solid in a liquid-solid mixture settles to the bottom of the container, the liquid can be carefully poured off (decanted). A centrifuge (Figure 1-9(b)) can be used to separate some solid-liquid mixtures, such as those in blood. Another technique, called paper chromatography, can be used to separate mixtures of dyes or pigments because the different substances will move at different rates on the paper (Figure 1-9(c)).

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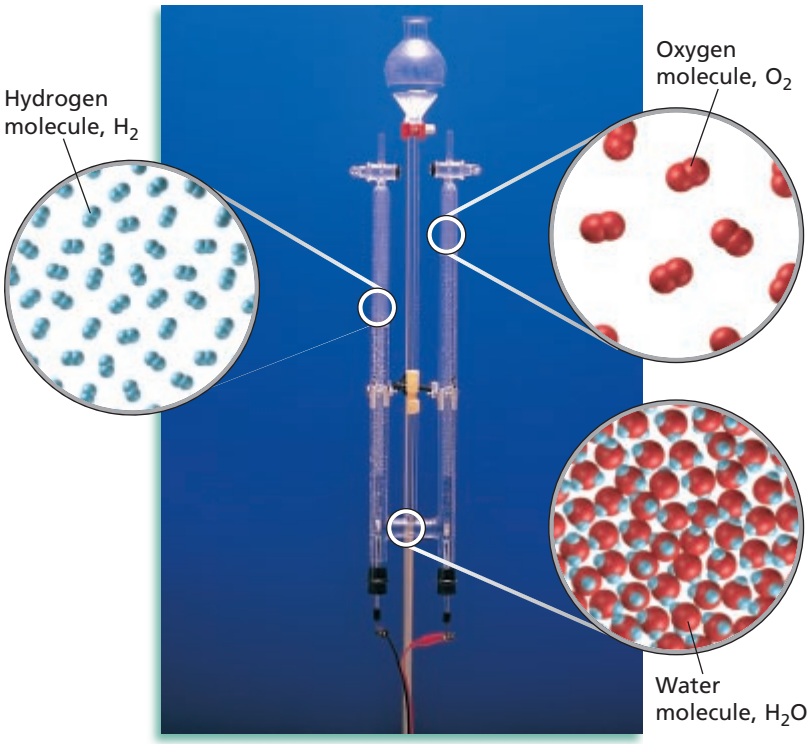
Pure Substances

In contrast to a mixture, a pure substance is homogenous as a single entity. *A* **pure substance** *has a fixed composition and differs from a mixture in the following ways:*

1. *Every sample of a given pure substance has exactly the same characteristic properties.* All samples of a pure substance have the same characteristic physical and chemical properties. These properties are so specific that they can be used to identify the substance. In contrast, the properties of a mixture depend on the relative amounts of the mixture's components.
2. *Every sample of a given pure substance has exactly the same composition.* Unlike mixtures, all samples of a pure substance have the same makeup. For example, pure water is always 11.2% hydrogen and 88.8% oxygen by mass.

Pure substances are either compounds or elements. A compound can be decomposed, or broken down, into two or more simpler compounds or elements by a chemical change. Water is a compound made of hydrogen and oxygen chemically bonded to form a single substance. Water can be broken down into hydrogen and oxygen through a chemical reaction called electrolysis, as shown in Figure 1-10(a).

Sucrose is made of carbon, hydrogen, and oxygen. Sucrose breaks down to form the other substances shown in Figure 1-10(b). Under intense heating, sucrose breaks down to produce carbon and water.



(a)

(b)

FIGURE 1-10 (a) Passing an electric current through water causes the compound to break down into the elements hydrogen and oxygen, which differ in composition from water. (b) When sucrose is heated, it caramelizes. When it is heated to a high temperature, it breaks down completely into carbon and water.

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TABLE 1-1 *Some Grades of Chemical Purity*

Increasing purity ↑

Primary standard reagents
ACS (American Chemical Society–specified reagents)
USP (United States Pharmacopoeia standards)
CP (chemically pure; purer than technical grade)
NF (National Formulary specifications)
FCC (Food Chemical Code specifications)
Technical (industrial chemicals)

Zinc Nitrate
CERTIFIED A.C.S.
$Zn(NO_3)_2 \cdot 6H_2O$ F.W. 297.47
Certificate of Actual Lot Analysis
Acidity (as HNO_3) 0.008%
Alkalies and Earths 0.02%
Chloride (Cl) 0.005%
Insoluble Matter 0.001%
Iron (Fe) 0.0002%
Lead (Pb) 0.001%
Phosphate (PO_4) 0.0002%
Sulfate (SO_4) 0.002%
Store separately from and avoid contact with combustible materials. Keep container closed and in a cool, dry place. Avoid contact with skin, eyes and clothing.
LOT NO. 917356
FL-02-0588
CAS 10196-18-6

FIGURE 1-11 The labeling on a reagent bottle lists the grade of the reagent and the percentages of impurities for that grade. What grade is this chemical?

Laboratory Chemicals and Purity

The chemicals in laboratories are generally treated as if they are pure. However, all chemicals have some impurities. Chemical grades of purity are listed in Table 1-1. The purity ranking of the grades can vary when agencies differ in their standards. For some chemicals, the USP grade may specify higher purity than the CP grade. For other chemicals, the opposite may be true. However, the primary standard reagent grade is always purer than the technical grade for the same chemical. Chemists need to be aware of the kinds of impurities in a reagent because these impurities could affect the results of a reaction. For example, the chemical label shown in Figure 1-11 shows the impurities for that grade. The chemical manufacturer must ensure that the standards set for that reagent by the American Chemical Society are met.

SECTION REVIEW

1. a. What is the main difference between physical properties and chemical properties?
   b. Give an example of each.
2. Classify each of the following as either a physical change or a chemical change.
   a. tearing a sheet of paper
   b. melting a piece of wax
   c. burning a log
3. You are given a sample of matter to examine. How do you decide whether the sample is a solid, liquid, or gas?
4. Contrast mixtures with pure substances.

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Secrets of the Cremona Violins

What are the most beautiful sounding of all violins? Most professionals will pick the instruments created in Cremona, Italy, following the Renaissance. At that time, Antonio Stradivari, the Guarneri family, and other designers created instruments of extraordinary sound that have yet to be matched. The craftsmen were notoriously secretive about their techniques, but, based on 20 years of research, Dr. Joseph Nagyvary, a professor of biochemistry at Texas A&M University, thinks he has discovered the key to the violins' sound hidden in the chemistry of their materials.

According to Dr. Nagyvary, Stradivarius instruments are nearly free of the shrill, high-pitched noises produced by modern violins. Generally, violin makers attribute this to the design of the instrument, but Dr. Nagyvary traces it to a different source. In Stradivari's day, wood for the violins was transported by floating it down a river from the mountains to Venice, where it was stored in sea water. Dr. Nagyvary first theorized that the soaking process could have removed ingredients from the wood that made it inherently noisy. His experiments revealed that microbes and minerals also permeated the wood, making their own contribution to the mellow musical sound.

Dr. Nagyvary and his violin

Dr. Nagyvary found other clues to the sound of the violins in the work of Renaissance alchemists. Aside from trying to turn lead into gold, alchemists made many useful experiments, including investigating different chemical means of preserving wood in musical instruments. Attempting to duplicate their techniques and to reproduce the effects of sea water, Dr. Nagyvary soaks all his wood in a "secret" solution. One of his favorite ingredients is a cherry-and-plum puree, which contains an enzyme called pectinase. The pectinase softens the wood, making it resonate more freely.

"The other key factor in a violin's sound," says Dr. Nagyvary, "is the finish, which is the filler and the varnish covering the instrument. Most modern finishes are made from rubbery materials, which limit the vibrations of the wood." Modern analysis has revealed that the Cremona finish was different: it was a brittle mineral microcomposite of a very sophisticated nature. According to historical accounts, all violin makers, including Stradivari, procured their varnishes from the local drugstore chemist, and they didn't even know what they were using! Dr. Nagyvary thinks this unknown and unsung drugstore chemist could have been the major factor behind the masterpieces for which violin makers like Stradivari received exclusive credit. By now, Dr. Nagyvary and his co-workers have identified most of the key ingredients of the Cremona finish.

Many new violins made from the treated wood and replicated finish have been made, and their sound has been analyzed by modern signal analyzers. These violins have been favorably compared with authentic Stradivari violins.

A number of expert violinists have praised the sound of Dr. Nagyvary's instruments, but some violin makers remain skeptical of the chemist's claims. They insist that it takes many years to reveal just how good a violin is. In the meantime, most everyone agrees that the art and science of violin making are still epitomized by the instruments of Cremona.

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SECTION 1-3

Elements

Objectives

- Use a periodic table to name elements, given their symbols.
- Use a periodic table to write the symbols of elements, given their names.
- Describe the arrangement of the periodic table.
- List the characteristics that distinguish metals, nonmetals, and metalloids.

As you have read, elements are pure substances that cannot be decomposed by chemical changes. The elements serve as the building blocks of matter. Each element has characteristic properties. The elements are organized into groups based on similar chemical properties. This organization of elements is the *periodic table,* which is shown in Figure 1-12 on the next page.

Introduction to the Periodic Table

Each small square of the periodic table shows the name of one element and the letter symbol for the element. For example, the first square, at the upper left, represents element 1, hydrogen, which has the atomic symbol H.

As you look through the table, you will see many familiar elements, including iron, sodium, neon, silver, copper, aluminum, sulfur, and lead. You can often relate the symbols to the English names of the elements. Though some symbols are derived from the element's older name, which was often in Latin, wolfram comes from the German name for tungsten. Table 1-2 lists some of those elements.

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TABLE 1-2 ***Elements with Symbols Based on Older Names***

Modern name	Symbol	Older name
Antimony	Sb	stibium
Copper	Cu	cuprum
Gold	Au	aurum
Iron	Fe	ferrum
Lead	Pb	plumbum
Mercury	Hg	hydrargyrum
Potassium	K	kalium
Silver	Ag	argentum
Sodium	Na	natrium
Tin	Sn	stannum
Tungsten	W	wolfram

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Periodic Table

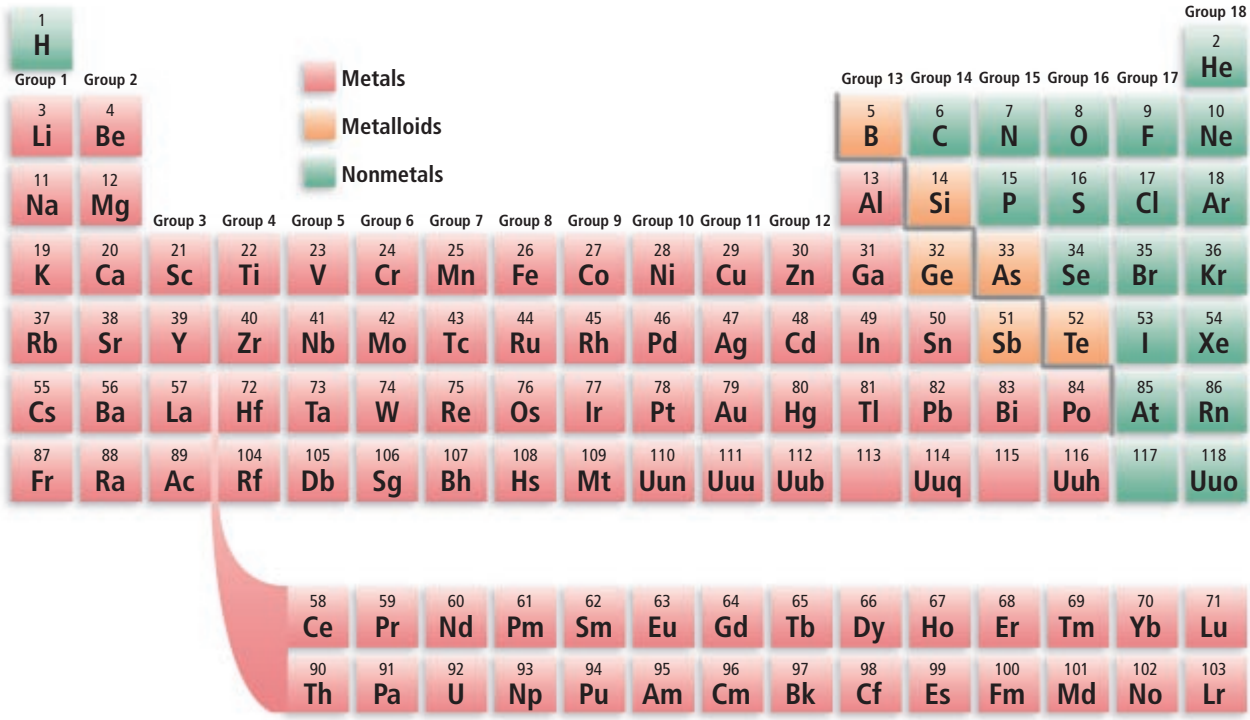

FIGURE 1-12 The periodic table of elements. The names of the elements can be found on Table A-6 in the appendix, pages 896–897.

The vertical columns of the periodic table are called **groups,** or **families.** Notice that they are numbered from 1 to 18 from left to right. Each group contains elements with similar chemical properties. For example, the elements in Group 2 are beryllium, magnesium, calcium, strontium, barium, and radium. All of these elements are reactive metals with similar abilities to bond to other kinds of atoms. The two major categories of elements are metals and nonmetals. Metalloids have properties intermediate between those of metals and nonmetals.

The horizontal rows of elements in the periodic table are called **periods.** Physical and chemical properties change somewhat regularly across a period. Elements that are close to each other in the same period tend to be more similar than elements that are farther apart. For example, in Period 2, the elements lithium and beryllium, in Groups 1 and 2, respectively, are somewhat similar in properties. However, their properties are very different from the properties of fluorine, the Period-2 element in Group 17.

The two sets of elements placed below the periodic table make up what are called the lanthanide series and the actinide series. These metallic elements fit into the table just after elements 57 and 89. They are placed below the table to keep the table from being too wide.

There is a section in the back of this book called the *Elements Handbook,* pages 726–783, which covers some representative elements in greater detail. You will use information from the handbook to complete the questions in the Handbook Search sections in the chapter reviews.

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Types of Elements

The periodic table is broadly divided into two main sections: metals and nonmetals. As you can see in Figure 1-12, the metals are at the left and in the center of the table. The nonmetals are toward the right. The elements along the dividing line show characteristics of both metals and nonmetals.

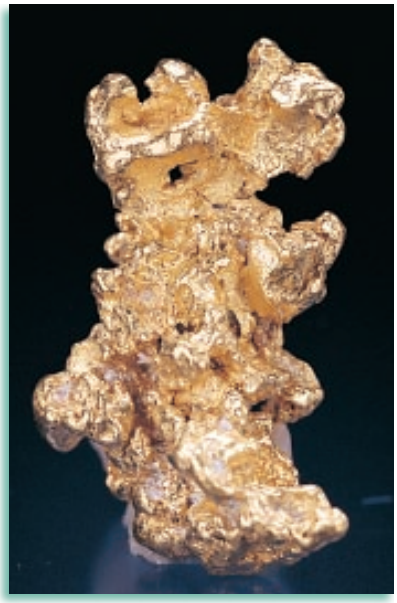
Metals

Some of the properties of metals may be familiar to you. For example, you can recognize metals by their shininess, or metallic luster. Perhaps the most important characteristic property of metals is the ease with which they conduct heat and electricity. Thus, *a* **metal** *is an element that is a good conductor of heat and electricity*.

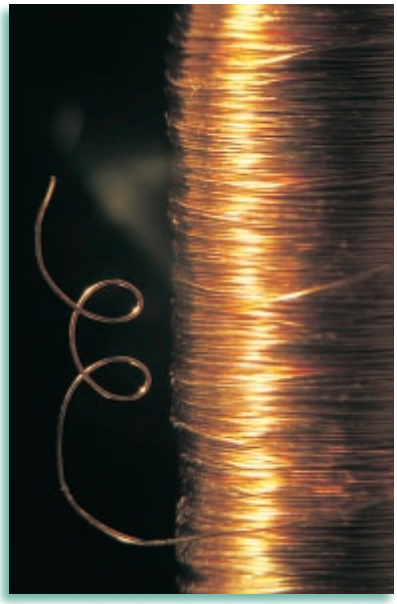
At room temperature, most metals are solids. Most metals also have the property of *malleability,* that is, they can be hammered or rolled into thin sheets. Metals also tend to be *ductile,* which means that they can be drawn into a fine wire. Metals behave this way because they have high *tensile strength,* the ability to resist breaking when pulled.

Although all metals conduct electricity well, metals also have very diverse properties. Mercury is a liquid at room temperature, whereas tungsten has the highest melting point of any element. The metals in Group 1 are so soft that they can be cut with a knife, yet others, like chromium, are very hard. Some metals, such as manganese and bismuth, are very brittle, yet others, such as iron and copper, are very malleable and ductile. Most metals have a silvery or grayish white *luster*. Two exceptions are gold and copper, which are yellow and reddish brown, respectively. Figure 1-13 shows examples of metals.

FIGURE 1-13 (a) Gold has a low reactivity, which is why it may be found in nature in relatively pure form. (b) Copper is used in wiring because it is ductile and is an excellent conductor of electricity. (c) Aluminum is malleable. It can be rolled into foil that is used for wrapping food.



(a)



(b)

(c)

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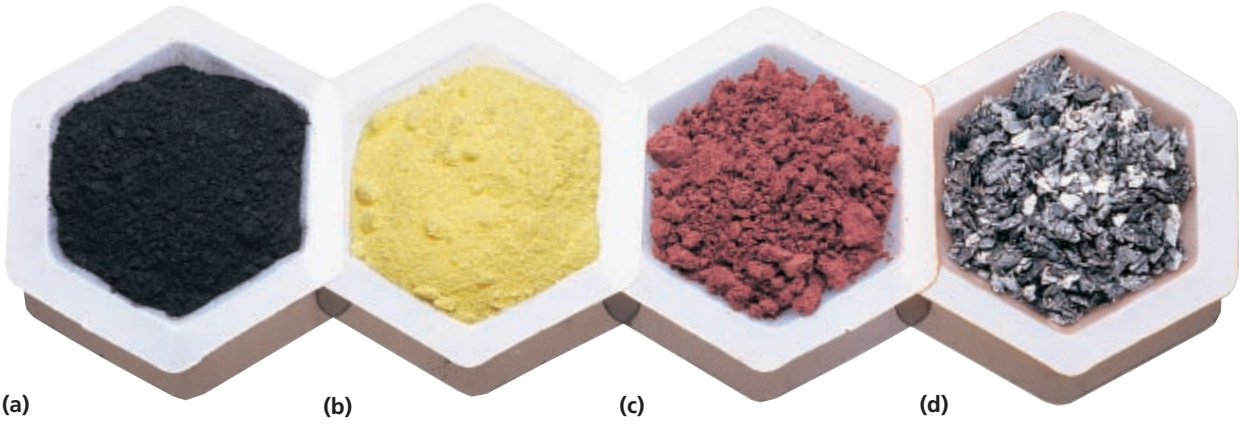

FIGURE 1-14 Various nonmetallic elements: (a) carbon, (b) sulfur, (c) phosphorus, and (d) iodine

Copper: A Representative Metal

Copper has a characteristic reddish color and a metallic luster. It is found naturally in minerals such as chalcopyrite and malachite. Pure copper melts at 1083°C and boils at 2567°C. It can be readily drawn into fine wire, pressed into thin sheets, and formed into tubing. Copper conducts electricity with little loss of energy.

Copper remains unchanged in pure, dry air at room temperature. When heated, it reacts with oxygen in air. It also reacts with sulfur and the elements in Group 17 of the periodic table. The green coating on a piece of weathered copper comes from the reaction of copper with oxygen, carbon dioxide, and sulfur compounds. Copper is an essential mineral in the human diet.

Nonmetals

Many nonmetals are gases at room temperature. These include nitrogen, oxygen, fluorine, and chlorine. One nonmetal, bromine, is a liquid. The solid nonmetals include carbon, phosphorus, selenium, sulfur, and iodine. These solids tend to be brittle rather than malleable and ductile. Some nonmetals are illustrated in Figure 1-14.

Low conductivity can be used to define nonmetals. *A* **nonmetal** *is an element that is a poor conductor of heat and electricity.* If you look at Figure 1-12, you will see that there are fewer nonmetals than metals.

Phosphorus: A Representative Nonmetal

Phosphorus is one of five solid nonmetals. Pure phosphorus is known in two common forms. Red phosphorus is a dark red powder that melts at 597°C. White phosphorus is a waxy solid that melts at 44°C. Because it ignites in air, white phosphorus is stored underwater.

Phosphorus is too reactive to exist in pure form in nature. It is present in huge quantities in phosphate rock, where it is combined with oxygen and calcium. All living things contain phosphorus.

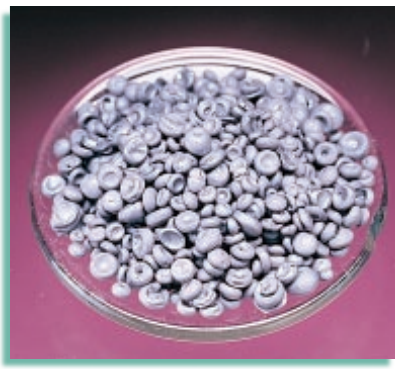

FIGURE 1-15 Selenium is a nonmetal, though it looks metallic.

Metalloids

A stair-step line separates the metals from the nonmetals on the periodic table. Several of the elements in the vicinity of this line are often

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FIGURE 1-16 The noble gases helium, neon, argon, krypton, and xenon are all used to make lighted signs of various colors.

referred to as metalloids. *A* **metalloid** *is an element that has some characteristics of metals and some characteristics of nonmetals.* All metalloids are solids at room temperature. They tend to be less malleable than metals but not as brittle as nonmetals. Some metalloids, such as antimony, have a somewhat metallic luster.

Metalloids tend to be semiconductors of electricity. That is, their ability to conduct electricity is intermediate between that of metals and that of nonmetals. Metalloids are used in the semiconducting materials found in desktop computers, hand-held calculators, digital watches, televisions, and radios.

Noble Gases

The elements in Group 18 of the periodic table are the noble gases. These elements are generally unreactive. In fact, prior to 1962 no noble gas compounds had been identified. That year, the first noble gas compound, xenon tetrafluoride, was prepared. Their low reactivity sets noble gases apart from the other families of elements. Group-18 elements are gases at room temperature. Neon, argon, krypton, and xenon are all used in lighting. Helium is used in party balloons and weather balloons because it is less dense than air.

SECTION REVIEW

1. Use the periodic table on the inside back cover to write the names for the elements that have the following symbols: O, S, Cu, Ag.
2. Use the periodic table to write the symbols for the following elements: iron, nitrogen, calcium, mercury.
3. Which elements are most likely to undergo the same kinds of reactions, those in a group or those in a period?
4. Describe the main differences between metals, nonmetals, and metalloids.

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CHAPTER 1 REVIEW

CHAPTER SUMMARY

1-1

- Chemistry is the study of the composition, structure, and properties of matter and its changes.
- Chemistry is classified as physical science. Six areas of study in chemistry are organic chemistry, inorganic chemistry, physical chemistry, analytical chemistry, biochemistry, and theoretical chemistry.
- A chemical is any substance that has a definite composition or is used or produced in a chemical process.
- Basic research is carried out for the sake of increasing knowledge. Applied research is carried out to solve practical problems. Technological development involves the use of existing knowledge to make life easier or more convenient.

Vocabulary

chemical (6)
chemistry (5)

1-2

- All matter has mass and takes up space. Mass is one measure of the amount of matter.
- An element is composed of one kind of atom. Compounds are made from two or more elements in fixed proportions.
- All substances have characteristic properties that enable chemists to tell the substances apart and to separate them.
- The physical properties of a substance can be observed or measured without changing the identity of the substance. Physical changes do not involve changes in identity.
- The three major states of matter are solid, liquid, and gas. The particles in these states differ in proximity to one another and ease of flow. Changes of state, such as melting and boiling, are physical changes.
- Chemical properties refer to a substance's ability to undergo changes that alter its composition and identity. Chemical changes, or chemical reactions, involve changes in identity.
- Energy changes accompany physical and chemical changes. Energy may be released or absorbed, but it is neither created nor destroyed.
- Matter can be classified into mixtures and pure substances. Pure substances differ from mixtures in that they have a definite composition that does not vary. Solutions are homogeneous mixtures.

Vocabulary

atom (10)
change of state (12)
chemical change (13)
chemical property (12)
chemical reaction (13)
compound (11)
element (10)
extensive property (11)
gas (12)
heterogeneous (16)
homogeneous (16)
intensive property (11)
liquid (12)
mass (10)
matter (10)
mixture (15)
physical change (12)
physical property (11)
plasma (12)
product (13)
pure substance (17)
reactant (13)
solid (12)
solution (16)

1-3

- Each element has a unique symbol. The periodic table shows the elements organized by their chemical properties. Columns on the table represent groups or families of elements with similar chemical properties. Properties vary across the rows, or periods.
- The elements can be classified as metals, nonmetals, metalloids, and noble gases. These classes occupy different areas of the periodic table. Metals tend to be shiny, malleable, ductile, and good conductors. Nonmetals tend to be brittle and poor conductors. Metalloids are intermediate in properties between metals and nonmetals, and they tend to be semiconductors of electricity. The noble gases are generally unreactive elements.

Vocabulary

family (21)
group (21)
metal (22)
metalloid (24)
nonmetal (23)
period (21)

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REVIEWING CONCEPTS

1. What is chemistry? (1-1)

2. What branch of chemistry is most concerned with the study of carbon compounds? (1-1)

3. What is meant by the word *chemical*, as used by scientists? (1-1)

4. Briefly describe the differences between basic research, applied research, and technological development. Provide an example of each. (1-1)

5. a. What is mass?
b. What is volume? (1-2)

6. How does the composition of a pure compound differ from that of a mixture? (1-2)

7. a. Define *property*.
b. How are properties useful in classifying materials? (1-2)

8. What is the difference between extensive properties and intensive properties? (1-2)

9. a. Define *physical property*.
b. List two examples of physical properties. (1-2)

10. a. Define *chemical property*.
b. List two examples of chemical properties. (1-2)

11. Distinguish between a *physical change* and a *chemical change*. (1-2)

12. a. How does a solid differ from a liquid?
b. How does a liquid differ from a gas?
c. How is a liquid similar to a gas?
d. What is a plasma? (1-2)

13. What is meant by a change in state? (1-2)

14. What is the significance of the vertical columns of the periodic table? What is the significance of the horizontal rows? (1-3)

15. Compare the physical properties of metals, nonmetals, metalloids, and noble gases and describe where in the periodic table each of these kinds of elements is located. (1-3)

16. In which of the six branches of chemistry would a scientist be working if he or she were doing the following: (1-1)
a. investigating energy relationships for various reactions
b. comparing properties of alcohols with those of sugars
c. studying reactions that occur during the digestion of food
d. carrying out tests to identify unknown substances

17. Identify the reactants and products in the following reaction: (1-2)
potassium + water ⟶ potassium hydroxide + hydrogen

18. Suppose element *X* is a poor conductor of electricity and breaks when hit with a hammer. Element *Z* is a good conductor of electricity and heat. In what area of the periodic table does each element most likely belong? (1-3)

19. Identify each of the following as either a physical change or a chemical change. Explain your answers. (1-2)
a. A piece of wood is sawed in half.
b. Milk turns sour.
c. Melted butter solidifies in the refrigerator.

20. Use the periodic table to write the names of the elements that have the following symbols, and identify each as a metal, nonmetal, metalloid, or noble gas. (1-3)
a. K
b. Ag
c. Si
d. Na
e. Hg
f. He

21. An unknown element is shiny and is found to be a good conductor of electricity. What other properties would you predict for it? (1-3)

22. Identify each of the following as an example of either basic research, applied research, or technological development: (1-1)
a. A new type of refrigerant is developed that is less damaging to the environment.
b. A new element is synthesized in a particle accelerator.
c. A computer chip is redesigned to increase the speed of the computer.

23. Use the periodic table to identify the group numbers and period numbers of the following elements: (1-3)
a. carbon, C
b. argon, Ar
c. chromium, Cr
d. barium, Ba

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24. a. Suppose different parts of a sample material have different compositions. What can you conclude about the material? (1-2)

b. Suppose different parts of a sample have the same composition. What can you conclude about the material? Explain your answer. (1-2)

TECHNOLOGY & LEARNING

25. **Graphing Calculator** Graphing Tabular Data

The graphing calculator can run a program that graphs ordered pairs of data, such as temperature versus time. In this problem you will learn how to create a table of data. Then you will learn how to use the program to plot the data.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data sets and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that after creating the lists, you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data sets, answer these questions.

a. Approximately what would the temperature be at the 16-minute interval?

b. Between which two intervals did the temperature increase the most: between 6 and 7 minutes, between 5 and 6 minutes, or between 8 and 9 minutes?

c. If the graph extended to 20 minutes, what would you expect the temperature to be?

HANDBOOK SEARCH

26. Review the information on trace elements in the *Elements Handbook* in the back of this text.

a. What are the functions of trace elements in the body?

b. What transition metal plays an important role in oxygen transport throughout the body?

c. What two Group 1 elements are part of the electrolyte balance in the body?

RESEARCH & WRITING

27. Research any current technological product of your choosing. Find out about its manufacture and uses. Also find out about the basic research and applied research that made its development possible.

ALTERNATIVE ASSESSMENT

28. Make a list of all the changes that you see around you involving matter during a one-hour period. Note whether each change seems to be a physical change or a chemical change. Give reasons for your answers.

29. Make a concept map using at least 15 terms from the vocabulary lists. An introduction to concept mapping is found in Appendix B of this book.

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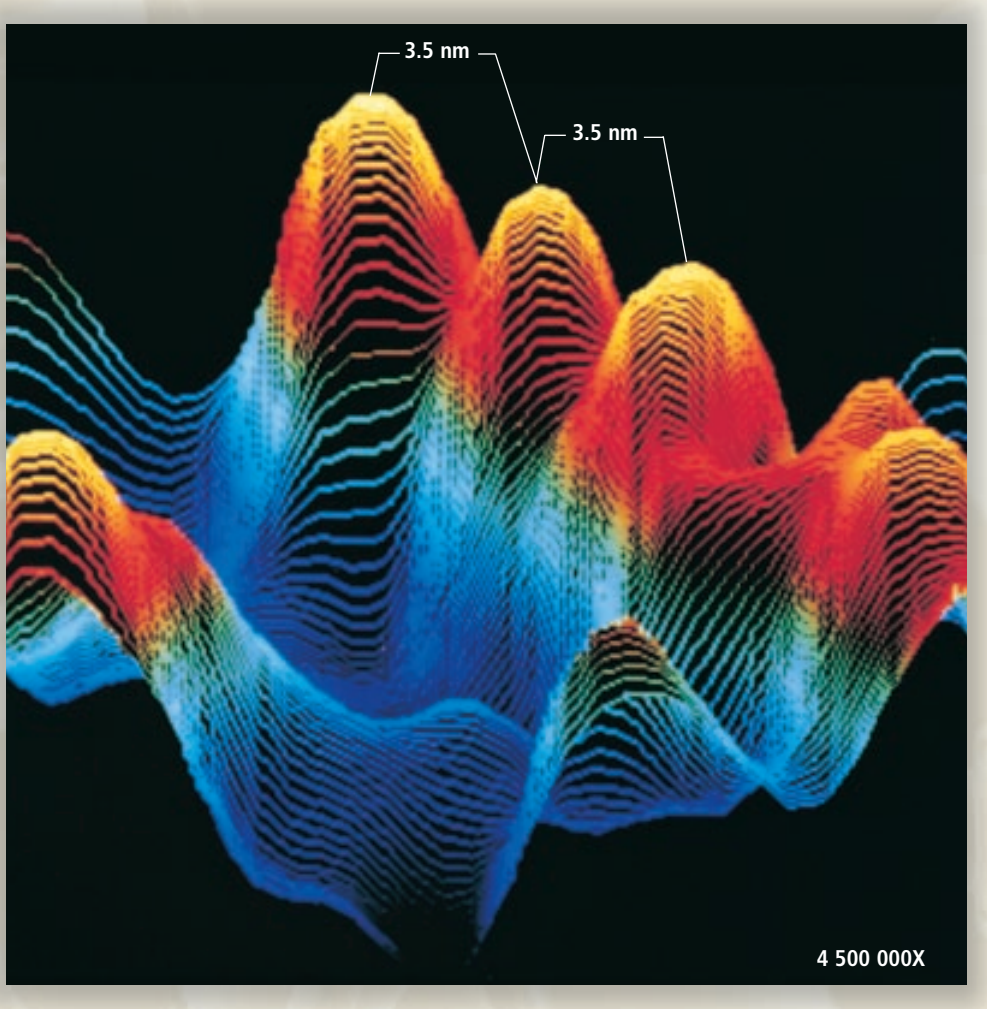
CHAPTER 2

Measurements and Calculations



Measurements provide quantitative information.

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Scientific Method

SECTION 2-1

Objectives

- Describe the purpose of the scientific method.
- Distinguish between qualitative and quantitative observations.
- Describe the differences between hypotheses, theories, and models.

Sometimes progress in science comes about through accidental discoveries. However, most scientific advances result from carefully planned investigations. The process researchers use to carry out their investigations is often called the scientific method. *The* **scientific method** *is a logical approach to solving problems by observing and collecting data, formulating hypotheses, testing hypotheses, and formulating theories that are supported by data.*

Observing and Collecting Data

Observing is the use of the senses to obtain information. Observation often involves making measurements and collecting data. The data may be descriptive (qualitative) or numerical (quantitative) in nature. Numerical information, such as the fact that a sample of copper ore has a mass of 25.7 grams, is *quantitative*. Non-numerical information, such as the fact that the sky is blue, is *qualitative*.

Experimenting involves carrying out a procedure under controlled conditions to make observations and collect data. To learn more about matter, chemists study systems. *A* **system** *is a specific portion of matter in a given region of space that has been selected for study during an experiment or observation.* When you observe a reaction in a test tube, the test tube and its contents form a system.

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FIGURE 2-1 These students are designing an experiment to determine how to get the largest volume of popped corn from a fixed number of kernels. They think that the volume is likely to increase as the moisture in the kernels increases. Their experiment will involve soaking some kernels in water and observing whether the volume of the popped corn is greater than that of corn popped from kernels that have not been soaked.

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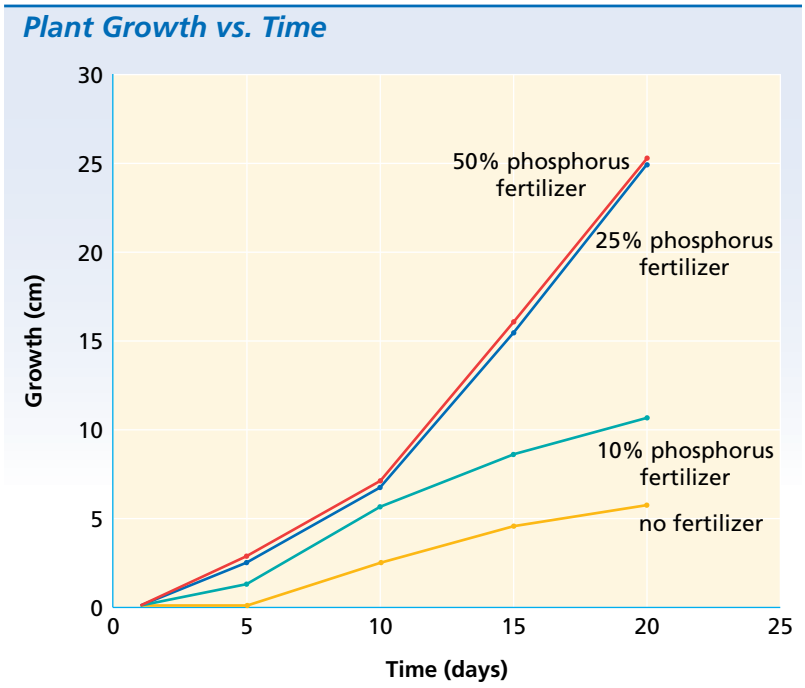

FIGURE 2-2 A graph of data can show relationships between two variables. In this case the graph shows data collected during an experiment to determine the effect of phosphorus fertilizer compounds on plant growth. The following is one possible hypothesis: *If* phosphorus stimulates corn-plant growth, *then* corn plants treated with a soluble phosphorus compound should grow faster, under the same conditions, than corn plants that are not treated.

Formulating Hypotheses

As scientists examine and compare the data from their own experiments, they attempt to find relationships and patterns—in other words, they make generalizations based on the data. Generalizations are statements that apply to a range of information. To make generalizations, data are sometimes organized in tables and analyzed using statistics or other mathematical techniques, often with the aid of graphs and a computer.

Scientists use generalizations about the data to formulate a **hypothesis,** *or testable statement*. The hypothesis serves as a basis for making predictions and for carrying out further experiments. Hypotheses are often drafted as "if-then" statements. The "then" part of the hypothesis is a prediction that is the basis for testing by experiment. Figure 2-2 shows data collected to test a hypothesis.

Testing Hypotheses

Testing a hypothesis requires experimentation that provides data to support or refute a hypothesis or theory. Do the data in Figure 2-2 support the hypothesis? If testing reveals that the predictions were not correct, the generalizations on which the predictions were based must be discarded or modified. One of the most difficult, yet most important, aspects of science is rejecting a hypothesis that is not supported by data.

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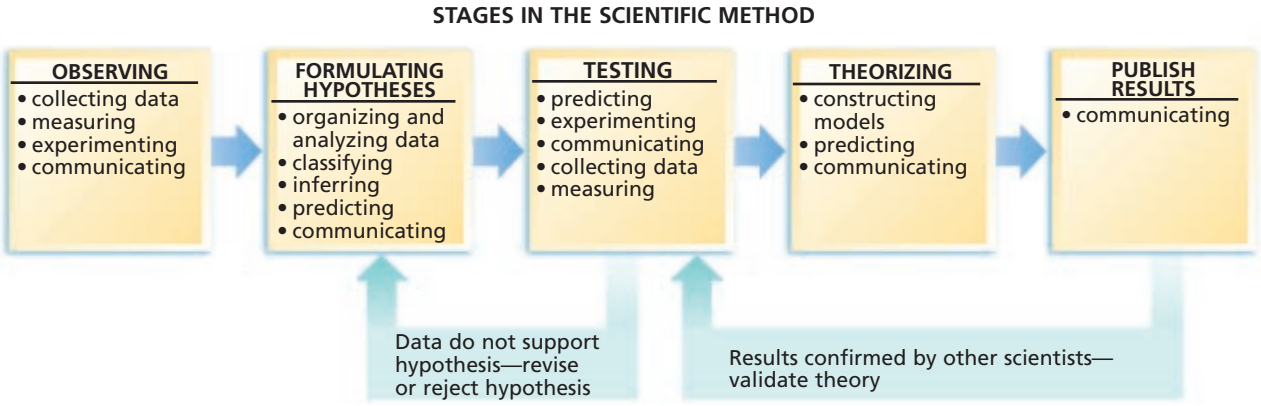

FIGURE 2-3 The scientific method is not a stepwise process. Scientists may repeat steps many times before there is sufficient evidence to formulate a theory. You can see that each stage represents a number of different activities.

Theorizing

When the data from experiments show that the predictions of the hypothesis are successful, scientists typically try to explain the phenomena they are studying by constructing a model. *A* **model** *in science is more than a physical object; it is often an explanation of how phenomena occur and how data or events are related*. Models may be visual, verbal, or mathematical. One of the most important models in chemistry is the atomic model of matter, which states that matter is composed of tiny particles called atoms.

If a model successfully explains many phenomena, it may become part of a theory. The atomic model is a part of the atomic theory, which you will study in Chapter 3. *A* **theory** *is a broad generalization that explains a body of facts or phenomena*. Theories are considered successful if they can predict the results of many new experiments. Examples of the important theories you will study in chemistry are kinetic-molecular theory and collision theory. Figure 2-3 shows where theory fits in the scheme of the scientific method.

SECTION REVIEW

1. What is the scientific method?
2. Which of the following are quantitative?
   a. the liquid floats on water
   b. the metal is malleable
   c. the liquid has a temperature of 55.6°C
3. How do hypotheses and theories differ?
4. How are models related to theories and hypotheses?
5. What are the components of the system in the graduated cylinder shown on page 38?

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Chemistry's Holy Grail

From *Chemistry Imagined, Reflections on Science,* written by Roald Hoffmann and illustrated by Vivian Torrence

In other fields the important questions seem to be breathtakingly simple: How does the brain work? Let's land a manned space craft on Mars . . . What is the "cure" for cancer? The outsider romanticizes, to be sure. But what about chemistry, where is the Holy Grail of the molecular science? . . .

To search for the Holy Grail, 150 of King Arthur's knights committed their hearts and resources. Translated to modern times, a like group effort demands some gigantic, or at least intricately expensive, machinery. Big science, in other words: a supercollider to search the innards, a space telescope to probe the outer fringes, a genome project to map human heredity. None of these is typical of chemistry, where from the beginning small groupings of people, working with relatively cheap cookware, have transformed a wondrous variety of matter.

Chemistry is an intermediate science. Its universe is defined not by reduction to a few elementary particles, or even to the hundred or so elements, but by a reaching out to the infinities of molecules that can be synthesized. A registry of new molecules contains over ten million man-made entries. A small fraction of these is of natural origin, though millions are waiting to be analyzed. And millions more are lost in species that our ecological pressure extinguishes. Most molecules are man- and woman-made. The beauty I would claim for chemistry is that of richness and complexity, the realm of the possible. There is no end to the range of structure and function that molecules exhibit. . . .

Roald Hoffmann

There is no Holy Grail in chemistry. Yes, we would like to have a magic machine that separates the most awful mixture, purifies every component to 99.4% purity (or better if we pay more) and determines the precise arrangement of atoms in space in each molecule. Yes, we'd like to know in complete detail the resistance of a molecule to every twist, bend, stretch, rock, and roll. And, yes, we certainly must espy the secret, rapid motions molecules undergo in their most intimate transformations. And, most of all, most fundamental to the science of transformations, we desire control—ways to synthesize to order, in a short time, using cheap materials, in one pot, any molecule in the world.

The secret of the Holy Grail is that it is to be found not in the consummation but in the search. Imagine every woman rejuvenated, every man saved, all ills, physical and mental, cured, all humanity perfect, and, of course, at peace. What a dull world! . . .

If the grand desires of chemistry were achieved—to know what one has, how things happen on the molecular scale, how to create molecules with absolute control—chemistry would simply vanish. To come to terms with complexity and the never-ending search, to find joy and beauty in the plain thing, the small step—that is the grail.

Reading for Meaning

What does Hoffmann mean when he says that chemistry is an intermediate science?

Read Further

Hoffmann states that, most of all, chemists desire ways to control chemical reactions. Research three ways that chemists control reactions, and write a paragraph describing each.

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Units of Measurement

SECTION 2-2

Objectives

- Distinguish between a quantity, a unit, and a measurement standard.
- Name SI units for length, mass, time, volume, and density.
- Distinguish between mass and weight.
- Perform density calculations.
- Transform a statement of equality to a conversion factor.

Measurements are quantitative information. A measurement is more than just a number, even in everyday life. Suppose a chef were to write a recipe listing quantities such as 1 salt, 3 sugar, and 2 flour. The cooks could not use the recipe without more information. They would need to know whether the number 3 represented teaspoons, tablespoons, cups, ounces, grams, or some other unit for sugar.

Measurements *represent* quantities. *A* **quantity** *is something that has magnitude, size, or amount.* A quantity is not the same as a measurement. For example, the quantity represented by a teaspoon is volume. The teaspoon is a unit of measurement, while volume is a quantity. A teaspoon is a measurement standard in this country. Units of measurement compare what is to be measured with a previously defined size. Nearly every measurement is a number plus a unit. The choice of unit depends on the quantity being measured.

Many centuries ago, people sometimes marked off distances in the number of foot lengths it took to cover the distance. But this system was unsatisfactory because the number of foot lengths used to express a distance varied with the size of the measurer's foot. Once there was agreement on a standard for foot length, confusion as to the real length was eliminated. It no longer mattered who made the measurement, as long as the standard measuring unit was correctly applied.

SI Measurement

Scientists all over the world have agreed on a single measurement system called *Le Système International d'Unités*, abbreviated **SI.** This system was adopted in 1960 by the General Conference on Weights and Measures. SI has seven base units, and most other units are derived from these seven. Some non-SI units are still commonly used by chemists and are also used in this book.

SI units are defined in terms of standards of measurement. The standards are objects or natural phenomena that are of constant value, easy to preserve and reproduce, and practical in size. International organizations monitor the defining process. In the United States, the National Institute of Standards and Technology plays the main role in maintaining standards and setting style conventions. For example, numbers are written in a form that is agreed upon internationally. The number seventy-five thousand is written 75 000, not 75,000, because the comma is used in other countries to represent a decimal point.

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TABLE 2-1 *SI Base Units*

Quantity	Quantity symbol	Unit name	Unit abbreviation	Defined standard
Length	l	meter	m	the length of the path traveled by light in a vacuum during a time interval of 1/299 792 458 of a second
Mass	m	kilogram	kg	the unit of mass equal to the mass of the international prototype of the kilogram
Time	t	second	s	the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom
Temperature	T	kelvin	K	the fraction 1/273.16 of the thermodynamic temperature of the triple point of water
Amount of substance	n	mole	mol	the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12
Electric current	I	ampere	A	the constant current which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross section, and placed 1 meter apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} newton per meter of length
Luminous intensity	I_v	candela	cd	the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540×10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian

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SI Base Units

The seven SI base units and their standard abbreviated symbols are listed in Table 2-1. All the other SI units can be derived from the fundamental units.

Prefixes added to the names of SI base units are used to represent quantities that are larger or smaller than the base units. Table 2-2 lists SI prefixes using units of length as examples. For example, the prefix *centi-*, abbreviated c, represents an exponential factor of 10^{-2}, which equals 1/100. Thus, 1 centimeter, 1 cm, equals 0.01 m, or 1/100 of a meter.

Mass

As you learned in Chapter 1, mass is a measure of the quantity of matter. The SI standard unit for mass is the kilogram. The standard for mass defined in Table 2-1 is used to calibrate balances all over the world.

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TABLE 2-2 *SI Prefixes*

Prefix	Unit abbreviation	Exponential factor	Meaning	Example
tera	T	10^{12}	1 000 000 000 000	1 terameter (Tm) = 1×10^{12} m
giga	G	10^{9}	1 000 000 000	1 gigometer (Gm) = 1×10^{9} m
mega	M	10^{6}	1 000 000	1 megameter (Mm) = 1×10^{6} m
kilo	k	10^{3}	1000	1 kilometer (km) = 1000 m
hecto	h	10^{2}	100	1 hectometer (hm) = 100 m
deka	da	10^{1}	10	1 dekameter (dam) = 10 m
		10^{0}	**1**	**1 meter (m)**
deci	d	10^{-1}	1/10	1 decimeter (dm) = 0.1 m
centi	c	10^{-2}	1/100	1 centimeter (cm) = 0.01 m
milli	m	10^{-3}	1/1000	1 millimeter (mm) = 0.001 m
micro	μ	10^{-6}	1/1 000 000	1 micrometer (μm) = 1×10^{-6} m
nano	n	10^{-9}	1/1 000 000 000	1 nanometer (nm) = 1×10^{-9} m
pico	p	10^{-12}	1/1 000 000 000 000	1 picometer (pm) = 1×10^{-12} m
femto	f	10^{-15}	1/1 000 000 000 000 000	1 femtometer (fm) = 1×10^{-15} m
atto	a	10^{-18}	1/1 000 000 000 000 000 000	1 attometer (am) = 1×10^{-18} m

The mass of a typical textbook is about 1 kg. The gram, g, which is 1/1000 of a kilogram, is more useful for measuring masses of small objects, such as flasks and beakers. For even smaller objects, such as tiny quantities of chemicals, the milligram, mg, is often used. One milligram is 1/1000 of a gram, or 1/1 000 000 of a kilogram.

Mass is often confused with weight because people often express the weight of an object in grams. Mass is determined by comparing the mass of an object with a set of standard masses that are part of the balance. **Weight** *is a measure of the gravitational pull on matter.* Unlike weight, mass does not depend on such an attraction. Mass is measured on instruments such as a balance, and weight is typically measured on a spring scale. Taking weight measurements involves reading the amount that an object pulls down on a spring. As the force of Earth's gravity on an object increases, the object's weight increases. The weight of an object on the moon is about one-sixth of its weight on Earth.

Length

The SI standard unit for length is the meter. A distance of 1 m is about the width of an average doorway. To express longer distances, the kilometer, km, is used. One kilometer equals 1000 m. Road signs in the United States sometimes show distances in kilometers as well as miles. The kilometer is the unit used to express highway distances in most other countries of the world. To express shorter distances, the centimeter

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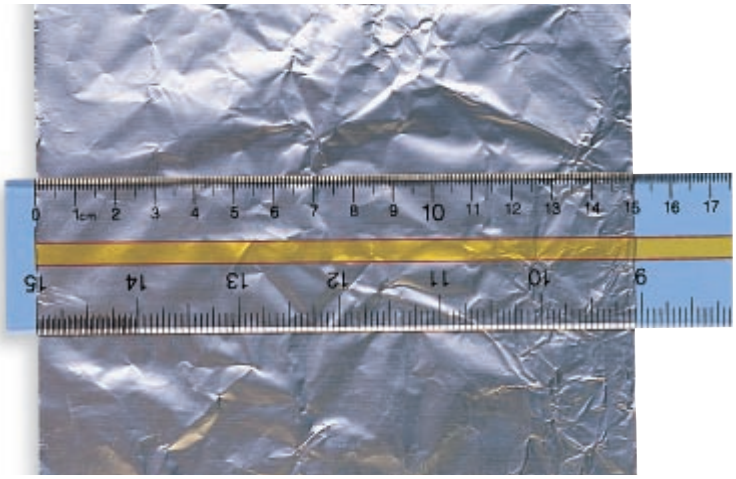
FIGURE 2-4 The meter is the SI unit of length, but the centimeter is often used to measure smaller distances. What is the width in cm of the rectangular piece of aluminum foil shown?



is often used. From Table 2-2, you can see that one centimeter equals 1/100 of a meter. The width of this book is just over 20 cm.

Derived SI Units

Many SI units are combinations of the quantities shown in Table 2-1. *Combinations of SI base units form* **derived units.** Some derived units are shown in Table 2-3.

Derived units are produced by multiplying or dividing standard units. For example, area, a derived unit, is length times width. If both length and width are expressed in meters, the area unit equals meters times meters, or square meters, abbreviated m^2. The last column of

TABLE 2-3 *Derived SI Units*

Quantity	Quantity symbol	Unit	Unit abbreviation	Derivation
Area	A	square meter	m^2	length × width
Volume	V	cubic meter	m^3	length × width × height
Density	D	kilograms per cubic meter	$\frac{kg}{m^3}$	$\frac{\text{mass}}{\text{volume}}$
Molar mass	M	kilograms per mole	$\frac{kg}{mol}$	$\frac{\text{mass}}{\text{amount of substance}}$
Concentration	c	moles per liter	M	$\frac{\text{amount of substance}}{\text{volume}}$
Molar volume	V_m	cubic meters per mole	$\frac{m^3}{mol}$	$\frac{\text{volume}}{\text{amount of substance}}$
Energy	E	joule	J	force × length

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Table 2-3 shows the combination of fundamental units used to obtain derived units.

Some combination units are given their own names. For example, pressure expressed in base units is the following.

$$kg/m \cdot s^2$$

The name *pascal,* Pa, is given to this combination. You will learn more about pressure in Chapter 10. Prefixes can also be added to express derived units. Area can be expressed in cm^2, square centimeters, or mm^2, square millimeters.

FIGURE 2-5 The speed that registers on a speedometer represents distance traveled per hour and is expressed in the derived units kilometers per hour or miles per hour.

Volume

Volume *is the amount of space occupied by an object.* The derived SI unit of volume is cubic meters, m^3. One cubic meter is equal to the volume of a cube whose edges are 1 m long. Such a large unit is inconvenient for expressing the volume of materials in a chemistry laboratory. Instead, a smaller unit, the cubic centimeter, cm^3, is often used. There are 100 centimeters in a meter, so a cubic meter contains 1 000 000 cm^3.

$$1\ m^3 \times \frac{100\ cm}{1\ m} \times \frac{100\ cm}{1\ m} \times \frac{100\ cm}{1\ m} = 1\ 000\ 000\ cm^3$$

When chemists measure the volumes of liquids and gases, they often use a non-SI unit called the liter. The liter is equivalent to one cubic decimeter. Thus, a liter, L, is also equivalent to 1000 cm^3. Another non-SI unit, the milliliter, mL, is used for smaller volumes. There are 1000 mL in 1 L. Because there are also 1000 cm^3 in a liter, the two units—milliliter and cubic centimeter—are interchangeable.

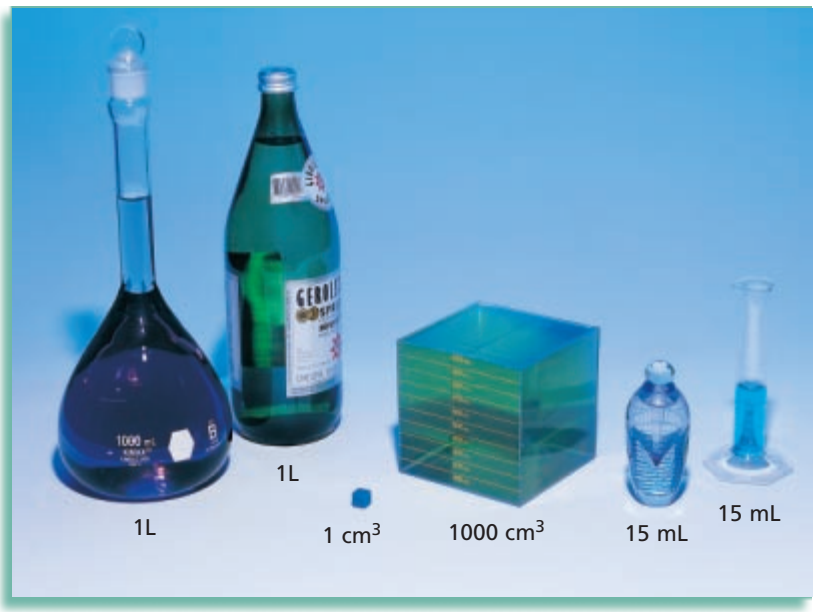

FIGURE 2-6 The relationships between various volumes are shown here. One liter contains 1000 mL of liquid, and 1 mL is equivalent to 1 cm^3. A small perfume bottle contains about 15 mL of liquid. The volumetric flask and graduated cylinder are used for measuring liquid volumes in the lab.

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FIGURE 2-7 Density is the ratio of mass to volume. Both water and copper shot float on mercury because mercury is more dense.

Density

An object made of cork feels lighter than a lead object of the same size. What you are actually comparing in such cases is how massive objects are compared with their size. This property is called density. **Density** *is the ratio of mass to volume, or mass divided by volume*. Mathematically, the relationship for density can be written in the following way.

$$density = \frac{mass}{volume} \text{ or } D = \frac{m}{V}$$

The quantity m is mass, V is volume, and D is density.

The SI unit for density is derived from the base units for mass and volume—the kilogram and the cubic meter, respectively—and can be expressed as kilograms per cubic meter, kg/m^3. This unit is inconveniently large for the density measurements you will make in the laboratory. You will often see density expressed in grams per cubic centimeter, g/cm^3, or grams per milliliter, g/mL. The densities of gases are generally reported either in kilograms per cubic meter, kg/m^3, or in grams per liter, g/L.

Density is a characteristic physical property of a substance. It does not depend on the size of the sample because as the sample's mass increases, its volume increases proportionately, and the ratio of mass to volume is constant. Therefore, density can be used as one property to help identify a substance. Table 2-4 shows the densities of some common materials. As you can see, cork has a density of only 0.24 g/cm^3, which is less than the density of liquid water. Because cork is less dense than water, it floats on water. Lead, on the other hand, has a density of 11.35 g/cm^3. The density of lead is greater than that of water, so lead sinks in water.

Note that Table 2-4 specifies the temperatures at which the densities were measured. That is because density varies with temperature. Most objects expand as temperature increases, thereby increasing in volume. Because density is mass divided by volume, density usually decreases with increasing temperature.

TABLE 2-4 *Densities of Some Familiar Materials*

Solids	Density at 20°C (g/cm^3)	Liquids	Density at 20°C (g/mL)
cork	0.24*	gasoline	0.67*
butter	0.86	ethyl alcohol	0.791
ice	0.92†	kerosene	0.82
sucrose	1.59	turpentine	0.87
bone	1.85*	water	0.998
diamond	3.26*	sea water	1.025**
copper	8.92	milk	1.031*
lead	11.35	mercury	13.6

† measured at 0°C
* typical density
** measured at 15°C

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Quick LAB

Density of Pennies

Wear Safety Goggles and an Apron.

Materials

- balance
- 100 mL graduated cylinder
- 40 pennies dated before 1982
- 40 pennies dated after 1982
- water

Procedure

1. Using the balance, determine the mass of the 40 pennies minted prior to 1982. Repeat this measurement two more times. Average the results of the three trials to determine the average mass of the pennies.
2. Repeat step 1 with the 40 pennies minted after 1982.
3. Pour about 50 mL of water into the 100 mL graduated cylinder. Record the exact volume of the water. Add the 40 pennies minted before 1982. Record the volume of the water and pennies. Repeat this process two more times. Determine the volume of the pennies for each trial. Average the results of those trials to determine the average volume of the pennies.
4. Repeat step 3 with the 40 pennies minted after 1982.
5. Review your data for any large differences between trials that could increase the error of your results. Repeat those measurements.
6. Use the average volume and average mass to calculate the average density for each group of pennies.
7. Compare the average calculated densities with the density of the copper listed in Table 2-4.

Discussion

1. Why is it best to use the results of three trials rather than a single trial for determining the density?
2. How did the densities of the two groups of pennies compare? How do you account for any difference?
3. Use the results of this investigation to formulate a hypothesis about the composition of the two groups of pennies. How could you test your hypothesis?

SAMPLE PROBLEM 2-1

A sample of aluminum metal has a mass of 8.4 g. The volume of the sample is 3.1 cm^3. Calculate the density of aluminum.

SOLUTION

Given: mass (m) = 8.4 g
volume (V) = 3.1 cm^3

Unknown: density (D)

$$density = \frac{mass}{volume} = \frac{8.4\ g}{3.1\ cm^3} = 2.7\ g/cm^3$$

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PRACTICE

1. What is the density of a block of marble that occupies 310 cm^3 and has a mass of 853 g?

   Answer 2.75 g/cm^3

2. Diamond has a density of 3.26 g/cm^3. What is the mass of a diamond that has a volume of 0.350 cm^3?

   Answer 1.14 g

3. What is the volume of a sample of liquid mercury that has a mass of 76.2 g, given that the density of mercury is 13.6 g/mL?

   Answer 5.60 mL

Conversion Factors

A **conversion factor** *is a ratio derived from the equality between two different units that can be used to convert from one unit to the other.* For example, suppose you want to know how many quarters there are in a certain number of dollars. To figure out the answer, you need to know how quarters and dollars are related. There are four quarters per dollar and one dollar for every four quarters. Those facts can be expressed as ratios in three conversion factors.

$$\frac{4 \text{ quarters}}{1 \text{ dollar}} = 1 \qquad \frac{1 \text{ dollar}}{4 \text{ quarters}} = 1 \qquad \frac{0.25 \text{ dollar}}{1 \text{ quarter}} = 1$$

Notice that each conversion factor equals 1. That is because the two quantities divided in any conversion factor are equivalent to each other—as in this case, where 4 quarters equal 1 dollar. Because conversion factors are equal to 1, they can be multiplied by other factors in equations without changing the validity of the equations. When you want to use a conversion factor to change a unit in a problem, you can set up the problem in the following way.

$$\text{quantity sought} = \text{quantity given} \times \text{conversion factor}$$

For example, to determine the number of quarters in 12 dollars, you would carry out the unit conversion that allows you to change from dollars to quarters.

$$\text{number of quarters} = 12 \text{ dollars} \times \text{conversion factor}$$

Next you would have to decide which conversion factor gives you an answer in the desired unit. In this case, you have dollars and you want quarters. To obtain quarters, you must divide the quantity by dollars. Therefore, the conversion factor in this case must have dollars in the denominator. That factor is 4 quarters/1 dollar. Thus, you would set up the calculation as follows.

$$? \text{ quarters} = 12 \text{ dollars} \times \text{conversion factor}$$

$$= 12 \cancel{\text{dollars}} \times \frac{4 \text{ quarters}}{1 \cancel{\text{dollar}}} = 48 \text{ quarters}$$

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Notice that the dollars have divided out, leaving an answer in the desired unit—quarters.

Suppose you had guessed wrong and used 1 dollar/4 quarters when choosing which of the two conversion factors to use. You would have an answer with entirely inappropriate units.

$$\text{? quarters} = 12 \text{ dollars} \times \frac{1 \text{ dollar}}{4 \text{ quarters}} = \frac{3 \text{ dollars}^2}{\text{quarter}}$$

You will work many problems in this book. It is always best to begin with an idea of the units you will need in your final answer. When working through the Sample Problems, keep track of the units needed for the unknown quantity. Check your final answer against what you've written as the unknown quantity.

Deriving Conversion Factors

You can derive conversion factors if you know the relationship between the unit you have and the unit you want. For example, from the fact that *deci-* means "1/10," you know that there is 1/10 of a meter per decimeter and that each meter must have 10 decimeters. Thus, from the equality

$$1 \text{ m} = 10 \text{ dm}$$

you can write the following conversion factors relating meters and decimeters.

$$\frac{1 \text{ m}}{10 \text{ dm}} \text{ and } \frac{0.1 \text{ m}}{\text{dm*}} \text{ and } \frac{10 \text{ dm}}{\text{m}}$$

The following sample problem illustrates an example of deriving conversion factors to make a unit conversion.

SAMPLE PROBLEM 2-2

Express a mass of 5.712 grams in milligrams and in kilograms.

SOLUTION

Given: 5.712 g
Unknown: mass in mg and kg

The expression that relates grams to milligrams is

$$1 \text{ g} = 1000 \text{ mg}$$

The possible conversion factors that can be written from this expression are

$$\frac{1000 \text{ mg}}{\text{g}} \text{ and } \frac{1 \text{ g}}{1000 \text{ mg}}$$

*In this book, when there is no digit shown in the denominator, you can assume the value is 1.

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To derive an answer in mg, you'll need to multiply 5.712 g by 1000 mg/g.

$$5.712 \text{ g} \times \frac{1000 \text{ mg}}{\text{g}} = 5712 \text{ mg}$$

This answer makes sense because milligrams is a smaller unit than grams and, therefore, there should be more of them.

The kilogram problem is solved similarly.

$$1 \text{ kg} = 1000 \text{ g}$$

Conversion factors representing this expression are

$$\frac{1 \text{ kg}}{1000 \text{ g}} \text{ and } \frac{1000 \text{ g}}{\text{kg}}$$

To derive an answer in kg, you'll need to multiply 5.712 g by 1 kg/1000 g.

$$5.712 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.005712 \text{ kg}$$

The answer makes sense because kilograms is a larger unit than grams and, therefore, there should be fewer of them.

PRACTICE

1. Express a length of 16.45 m in centimeters and in kilometers.

Answer
1645 cm, 0.01645 km

2. Express a mass of 0.014 mg in grams.

Answer
0.000 014 g

SECTION REVIEW

1. Why are standards needed for measured quantities?
2. Label each of the following measurements by the quantity each represents. For instance, a measurement of 10.6 kg/m^3 represents density.
   a. 5.0 g/mL
   b. 37 s
   c. 47 J
   d. 39.56 g
   e. 25.3 cm^3
   f. 325 ms
   g. 500 m^2
   h. 30.23 mL
   i. 2.7 mg
   j. 0.005 L
3. Complete the following conversions.
   a. 10.5 g = _____ kg
   b. 1.57 km = _____ m
   c. 3.54 µg = _____ g
   d. 3.5 mol = _____ µmol
   e. 1.2 L = _____ mL
   f. 358 cm^3 = _____ m^3
   g. 548.6 mL = _____ cm^3
4. Write conversion factors to represent the following equalities.
   a. 1 m^3 = 1 000 000 cm^3
   b. 1 in. = 2.54 cm
   c. 1 µg = 0.000 001 g
   d. 1 Mm = 1 000 000 m
5. a. What is the density of an 84.7 g sample of an unknown substance if the sample occupies 49.6 cm^3?
   b. What volume would be occupied by 7.75 g of this same substance?

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Roadside Pollution Detector

Dr. Donald Stedman, a chemist at the University of Denver, has developed a device that monitors exhaust emissions on highways.

The pollution detector sits on the side of a highway and shines a beam of infrared light across the road. After the beam passes through a car's exhaust fumes, it strikes a rotating mirror on the other side of the highway, which reflects the light onto four different sensors. These sensors detect changes in the infrared beam, and then each sensor uses that information to make different measurements. One detector gauges the amount of carbon dioxide in the exhaust. The second calculates the amount of carbon monoxide. A third sensor measures the amount of hydrocarbons, which contribute to the production of smog.

A car driving down the highway will break the infrared beam, then an exhaust reading is taken after the car passes for half a second to ensure that the beam measures data from the middle of the exhaust fumes.

A carbon monoxide rating of higher than 4.5% gets a poor rating on the display.

Stedman put the detector into action on a highway exit ramp in Denver. The device gives every car that drives by an emissions rating and automatically displays the rating on a nearby billboard. If less than 1.3% of the car's exhaust is carbon monoxide, it earns a "good" rating. A rating of less than 4.5% carbon monoxide receives a "fair" rating. A rating higher than 4.5% is a "poor" rating. Stedman has found that the billboard not only informs people that their cars are polluters but also motivates the drivers to get their cars fixed.

Stedman has determined that only a small percentage of cars are responsible for automobile pollution. In fact, half of all the pollution from automobiles is created by about 10% of the cars on the road.

Stedman adds that the drivers will share the economic benefits of cleaning up their act. "If you have a gross-polluting car," he says, "you will save the amount of money that the repair might cost you in your fuel economy in a couple of years because you get a tremendous 10 to 15% fuel-economy improvement by fixing a gross-polluting car."

1. *How does Dr. Stedman think his device will benefit society?*
2. *Why do you feel Dr. Stedman's research is important?*

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SECTION 2-3

Using Scientific Measurements

Objectives

- Distinguish between accuracy and precision.
- Determine the number of significant figures in measurements.
- Perform mathematical operations involving significant figures.
- Convert measurements into scientific notation.
- Distinguish between inversely and directly proportional relationships.

If you have ever measured something several times, you know that the results can vary. In science, for a reported measurement to be useful, there must be some indication of its reliability or uncertainty.

Accuracy and Precision

The terms *accuracy* and *precision* mean the same thing to most people. However, in science their meanings are quite distinct. **Accuracy** *refers to the closeness of measurements to the correct or accepted value of the quantity measured*. **Precision** *refers to the closeness of a set of measurements of the same quantity made in the same way*. Thus, measured values that are accurate are close to the accepted value. Measured values that are precise are close to one another but not necessarily close to the accepted value.

Figure 2-8 should help you visualize the difference between precision and accuracy. A set of darts thrown separately at a dartboard may land in various positions, relative to the bull's-eye and to one another. The

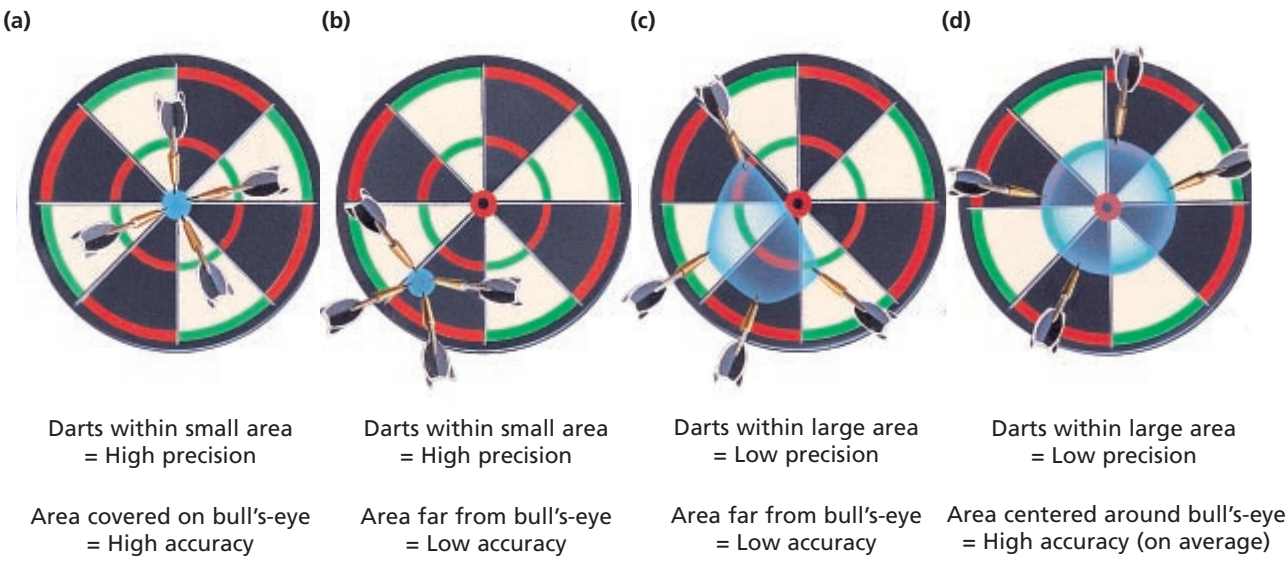
(a)
(b)
(c)
(d)
Darts within small area = High precision
Area covered on bull's-eye = High accuracy
Darts within small area = High precision
Area far from bull's-eye = Low accuracy
Darts within large area = Low precision
Area far from bull's-eye = Low accuracy
Darts within large area = Low precision
Area centered around bull's-eye = High accuracy (on average)

FIGURE 2-8 The sizes and locations of the areas covered by thrown darts illustrate the difference between precision and accuracy.

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closer the darts land to the bull's-eye, the more accurately they were thrown. The closer they land to one another, the more precisely they were thrown. Thus, the set of results shown in Figure 2-8(a) is both accurate and precise because the darts are close to the bull's-eye and close to each other. In Figure 2-8(b), the set of results is inaccurate but precise because the darts are far from the bull's-eye but close to each other. In Figure 2-8(c), the set of results is both inaccurate and imprecise because the darts are far from the bull's-eye and far from each other. Notice also that the darts are not evenly distributed around the bull's-eye, so the set, even considered on average, is inaccurate. In Figure 2-8(d), the set on average is accurate compared with the third case, but it is imprecise. That is because the darts are distributed evenly around the bull's-eye but are far from each other.

Percent Error

The accuracy of an individual value or of an average experimental value can be compared quantitatively with the correct or accepted value by calculating the percent error. **Percent error** *is calculated by subtracting the experimental value from the accepted value, dividing the difference by the accepted value, and then multiplying by 100.*

$$\text{Percent error} = \frac{\text{Value}_{accepted} - \text{Value}_{experimental}}{\text{Value}_{accepted}} \times 100$$

Percent error has a positive value if the accepted value is greater than the experimental value. It has a negative value if the accepted value is less than the experimental value. The following sample problem illustrates the concept of percent error.

SAMPLE PROBLEM 2-3

A student measures the mass and volume of a substance and calculates its density as 1.40 g/mL. The correct, or accepted, value of the density is 1.30 g/mL. What is the percent error of the student's measurement?

SOLUTION

$$\text{Percent error} = \frac{\text{Value}_{accepted} - \text{Value}_{experimental}}{\text{Value}_{accepted}} \times 100$$

$$= \frac{1.30\ \cancel{\text{g/mL}} - 1.40\ \cancel{\text{g/mL}}}{1.30\ \cancel{\text{g/mL}}} \times 100 = -7.7\%$$

PRACTICE

1. What is the percent error for a mass measurement of 17.7 g, given that the correct value is 21.2 g? *Answer* 17%
2. A volume is measured experimentally as 4.26 mL. What is the percent error, given that the correct value is 4.15 mL? *Answer* –2.7%

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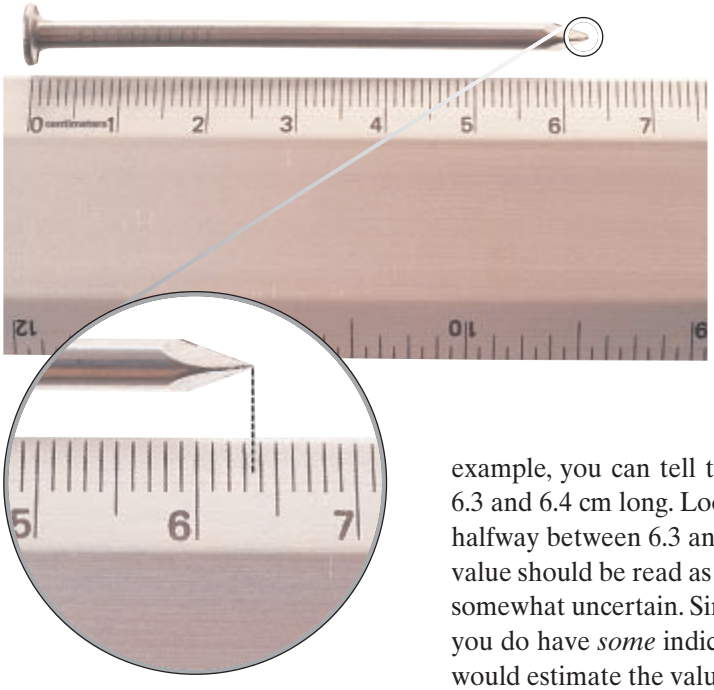

FIGURE 2-9 What value should be recorded for the length of this nail?

Error in Measurement

Some error or uncertainty always exists in any measurement. The skill of the measurer places limits on the reliability of results. The conditions of measurement also affect the outcome. The measuring instruments themselves place limitations on precision. Some balances can be read more precisely than others. The same is true of rulers, graduated cylinders, and other measuring devices.

When you use a properly calibrated measuring device, you can be almost certain of a particular number of digits in a reading. For example, you can tell that the nail in Figure 2-9 is definitely between 6.3 and 6.4 cm long. Looking more closely, you can see that the value is halfway between 6.3 and 6.4 cm. However, it is hard to tell whether the value should be read as 6.35 cm or 6.36 cm. The hundredths place is thus somewhat uncertain. Simply leaving it out would be misleading because you do have *some* indication of the value's likely range. Therefore, you would estimate the value to the final questionable digit, perhaps reporting the length of the nail as 6.36 cm. You might include a plus-or-minus value to express the range, for example, 6.36 cm ± 0.01 cm.

Significant Figures

In science, measured values are reported in terms of significant figures. **Significant figures** *in a measurement consist of all the digits known with certainty plus one final digit, which is somewhat uncertain or is estimated*. For example, in the reported nail length of 6.36 cm discussed above, the last digit, 6, is uncertain. All the digits, including the uncertain one, are significant, however. All contain information and are included in the reported value. Thus, the term *significant* does not mean *certain*. In any correctly reported measured value, the final digit is significant but not certain. Insignificant digits are never reported. As a chemistry student, you will need to use and recognize significant figures when you work with measured quantities and report your results, and when you evaluate measurements reported by others.

Determining the Number of Significant Figures

When you look at a measured quantity, you need to determine which digits are significant. That process is very easy if the number has no zeros because all the digits shown are significant. For example, if you see a number reported as 3.95, all three digits are significant. The significance of zeros in a number depends on their location, however. You need to learn and follow several rules involving zeros. After you have studied the rules in Table 2-5, use them to express the answers in the sample problem that follows.

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TABLE 2-5 *Rules for Determining Significant Zeros*

Rule	Examples
1. Zeros appearing between nonzero digits are significant.	a. 40.7 L has three significant figures. b. 87 009 km has five significant figures.
2. Zeros appearing in front of all nonzero digits are not significant.	a. 0.095 897 m has five significant figures. b. 0.0009 kg has one significant figure.
3. Zeros at the end of a number and to the right of a decimal point are significant.	a. 85.00 g has four significant figures. b. 9.000 000 000 mm has 10 significant figures.
4. Zeros at the end of a number but to the left of a decimal point may or may not be significant. If a zero has not been measured or estimated but is just a placeholder, it is not significant. A decimal point placed after zeros indicates that they are significant.	a. 2000 m may contain from one to four significant figures, depending on how many zeros are placeholders. **For measurements given in this text, assume that 2000 m has one significant figure.** b. 2000. m contains four significant figures, indicated by the presence of the decimal point.

SAMPLE PROBLEM 2-4

How many significant figures are in each of the following measurements?
a. 28.6 g
b. 3440. cm
c. 910 m
d. 0.046 04 L
e. 0.006 700 0 kg

SOLUTION

Determine the number of significant figures in each measurement using the rules listed in Table 2-5.

a. 28.6 g
There are no zeros, so all three digits are significant.

b. 3440. cm
By rule 4, the zero is significant because it is immediately followed by a decimal point; there are 4 significant figures.

c. 910 m
By rule 4, the zero is not significant; there are 2 significant figures.

d. 0.046 04 L
By rule 2, the first two zeros are not significant; by rule 1, the third zero is significant; there are 4 significant figures.

e. 0.006 700 0 kg
By rule 2, the first three zeros are not significant; by rule 3, the last three zeros are significant; there are 5 significant figures.

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PRACTICE

1. Determine the number of significant figures in each of the following.
   a. 804.05 g
   b. 0.014 403 0 km
   c. 1002 m
   d. 400 mL
   e. 30 000. cm
   f. 0.000 625 000 kg

Answer

1. a. 5
   b. 6
   c. 4
   d. 1
   e. 5
   f. 6

2. Suppose the value "seven thousand centimeters" is reported to you. How should the number be expressed if it is intended to contain the following?
   a. 1 significant figure
   b. 4 significant figures
   c. 6 significant figures

2. a. 7000 cm
   b. 7000. cm
   c. 7000.00 cm

Rounding

When you perform calculations involving measurements, you need to know how to handle significant figures. This is especially true when you are using a calculator to carry out mathematical operations. The answers given on a calculator can be derived results with more digits than are justified by the measurements.

Suppose you used a calculator to divide a measured value of 154 g by a measured value of 327 mL. Each of these values has three significant figures. The calculator would show a numerical answer of 0.470948012. The answer contains digits not justified by the measurements used to calculate it. Such an answer has to be rounded off to make its degree of certainty match that in the original measurements. The answer should be 0.471 g/mL.

The rules for rounding are shown in Table 2-6. The extent of rounding required in a given case depends on whether the numbers are being added, subtracted, multiplied, or divided.

TABLE 2-6 *Rules for Rounding Numbers*

If the digit following the last digit to be retained is:	then the last digit should:	Example (rounded to three significant figures)
greater than 5	be increased by 1	42.68 g ⟶ 42.7 g
less than 5	stay the same	17.32 m ⟶ 17.3 m
5, followed by nonzero digit(s)	be increased by 1	2.7851 cm ⟶ 2.79 cm
5, not followed by nonzero digit(s), and preceded by an odd digit	be increased by 1	4.635 kg ⟶ 4.64 kg (because 3 is odd)
5, not followed by nonzero digit(s), and the preceding significant digit is even	stay the same	78.65 mL ⟶ 78.6 mL (because 6 is even)

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Addition or Subtraction with Significant Figures

Consider two mass measurements, 25.1 g and 2.03 g. The first measurement, 25.1 g, has one digit to the right of the decimal point, in the tenths place. There is no information on possible values for the hundredths place. That place is simply blank and cannot be assumed to be zero. The other measurement, 2.03 g, has two digits to the right of the decimal point. It provides information up to and including the hundredths place.

Suppose you were asked to add the two measurements. Simply carrying out the addition would result in an answer of 25.1 g + 2.03 g = 27.13 g. That answer suggests there is certainty all the way to the hundredths place. However, that result is not justified because the hundredths place in 25.1 g is completely unknown. The answer must be adjusted to reflect the uncertainty in the numbers added.

When adding or subtracting decimals, the answer must have the same number of digits to the right of the decimal point as there are in the measurement having the fewest digits to the right of the decimal point. When working with whole numbers, the answer should be rounded so that the final digit is in the same place as the leftmost uncertain digit. Comparing the two values 25.1 g and 2.03 g, the measurement with the fewest digits to the right of the decimal point is 25.1 g. It has only one such digit. Following the rule, the answer must be rounded so that it has no more than one digit to the right of the decimal point. It should therefore be rounded to 27.1 g.

Multiplication and Division with Significant Figures

Suppose you calculated the density of an object that has a mass of 3.05 g and a volume of 8.47 mL. The following division on a calculator will give a value of 0.360094451.

$$density = \frac{mass}{volume} = \frac{3.05\ \text{g}}{8.47\ \text{mL}} = 0.360094451\ \text{g/mL}$$

The answer must be rounded to the correct number of significant figures. The values of mass and volume used to obtain the answer have only three significant figures each. The degree of certainty in the calculated result is not justified. *For multiplication or division, the answer can have no more significant figures than are in the measurement with the fewest number of significant figures.* In the calculation just described, the answer, 0.360094451 g/mL, would be rounded to three significant figures to match the significant figures in 8.47 mL and 3.05 g. The answer would thus be 0.360 g/mL.

SAMPLE PROBLEM 2-5

Carry out the following calculations. Express each answer to the correct number of significant figures.

a. 5.44 m – 2.6103 m

b. 2.4 g/mL × 15.82 mL

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SOLUTION Carry out each mathematical operation. Follow the rules in Table 2-5 and Table 2-6 for determining significant figures and for rounding.

a. The answer is rounded to 2.83 m (for subtraction there should be two digits to the right of the decimal point, to match 5.44 m).

b. The answer is rounded to 38 g (for multiplication there should be two significant figures in the answer, to match 2.4 g/mL).

PRACTICE

1. What is the sum of 2.099 g and 0.05681 g?

Answer
2.156 g

2. Calculate the quantity 87.3 cm – 1.655 cm.

Answer
85.6 cm

3. Calculate the area of a crystal surface that measures 1.34 µm by 0.7488 µm. (Hint: Recall that *area* = *length* × *width* and is measured in square units.)

Answer
1.00 μm^2

4. Polycarbonate plastic has a density of 1.2 g/cm^3. A photo frame is constructed from two 3.0 mm sheets of polycarbonate. Each sheet measures 28 cm by 22 cm. What is the mass of the photo frame?

Answer
440 g

Conversion Factors and Significant Figures

Earlier in this chapter, you learned how conversion factors are used to change one unit to another. Such conversion factors are typically exact. That is, there is no uncertainty in them. For example, there are exactly 100 cm in a meter. If you were to use the conversion factor 100 cm/m to change meters to centimeters, the 100 would not limit the degree of certainty in the answer. Thus, 4.608 m could be converted to centimeters as follows.

$$4.608\ \text{m} \times \frac{100\ \text{cm}}{\text{m}} = 460.8\ \text{cm}$$

The answer still has four significant figures. Because the conversion factor is considered exact, the answer would not be rounded. Most exact conversion factors are defined, rather than measured, quantities. Counted numbers also produce conversion factors of unlimited precision. For example, if you counted that there are 10 test tubes for every student, that would produce an exact conversion factor of 10 test tubes/student. There is no uncertainty in that factor.

Scientific Notation

In **scientific notation,** *numbers are written in the form* M × 10^n, *where the factor* M *is a number greater than or equal to 1 but less than 10 and* n *is a whole number.* For example, to write the quantity 65 000 km in

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scientific notation and show the first two digits as significant, you would write the following.

$$6.5 \times 10^4 \text{ km}$$

Writing the *M* factor as 6.5 shows that there are exactly two significant figures. If, instead, you intended the first three digits in 65 000 to be significant, you would write 6.50×10^4 km. When numbers are written in scientific notation, only the significant figures are shown.

Suppose you are expressing a very small quantity, such as the length of a flu virus. In ordinary notation this length could be 0.000 12 mm. That length can be expressed in scientific notation as follows.

$$0.000\,12 \text{ mm} = 1.2 \times 10^{-4} \text{ mm}$$

move the decimal point four places to the right and multiply the number by 10^{-4}

1. Determine *M* by moving the decimal point in the original number to the left or the right so that only one nonzero digit remains to the left of the decimal point.
2. Determine *n* by counting the number of places that you moved the decimal point. If you moved it to the left, *n* is positive. If you moved it to the right, *n* is negative.

Mathematical Operations Using Scientific Notation

1. *Addition and subtraction* These operations can be performed only if the values have the same exponent (*n* factor). If they do not, adjustments must be made to the values so that the exponents are equal. Once the exponents are equal, the *M* factors can be added or subtracted. The exponent of the answer can remain the same, or it may then require adjustment if the *M* factor of the answer has more than one digit to the left of the decimal point. Consider the example of the addition of 4.2×10^4 kg and 7.9×10^3 kg.

   We can make both exponents either 3 or 4. The following solutions are possible.

$$\begin{array}{r} 4.2 \times 10^4 \text{ kg} \\ +0.79 \times 10^4 \text{ kg} \\ \hline 4.99 \times 10^4 \text{ kg} \end{array} \quad \text{rounded to } 5.0 \times 10^4 \text{ kg}$$

or

$$\begin{array}{r} 7.9 \times 10^3 \text{ kg} \\ +42 \times 10^3 \text{ kg} \\ \hline 49.9 \times 10^3 \text{ kg} \end{array} = 4.99 \times 10^4 \text{ kg rounded to } 5.0 \times 10^4 \text{ kg}$$

   Note that the units remain kg throughout.

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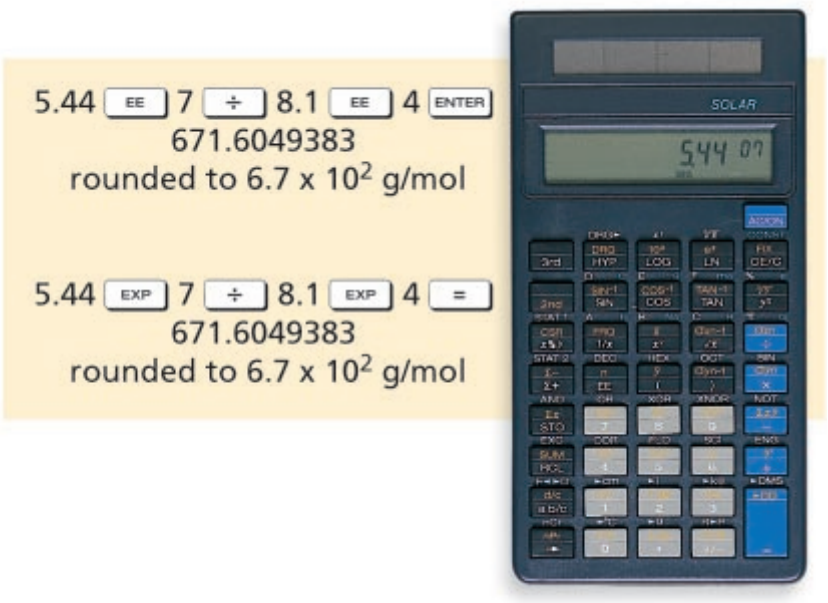

FIGURE 2-10 When you use a scientific calculator to work problems in scientific notation, don't forget to express the value on the display to the correct number of significant figures and show the units when you write the final answer.

2. *Multiplication* The *M* factors are multiplied, and the exponents are added algebraically.

Consider the multiplication of 5.23×10^{6} μm by 7.1×10^{-2} μm.

$$(5.23 \times 10^{6}\ \mu m)(7.1 \times 10^{-2}\ \mu m) = (5.23 \times 7.1)(10^{6} \times 10^{-2})$$
$$= 37.133 \times 10^{4}\ \mu m^{2} \text{ (adjust to two significant digits)}$$
$$= 3.7 \times 10^{5}\ \mu m^{2}$$

Note that when length measurements are multiplied, the result is area. The unit is now μm^2.

3. *Division* The *M* factors are divided, and the exponent of the denominator is subtracted from that of the numerator. The calculator keystrokes for this problem are shown in Figure 2-10.

$$\frac{5.44 \times 10^{7}\ g}{8.1 \times 10^{4}\ mol} = \frac{5.44}{8.1} \times 10^{7-4}\ g/mol$$
$$= 0.6716049383 \times 10^{3} \text{ (adjust to two significant figures)}$$
$$= 6.7 \times 10^{2}\ g/mol$$

Note that the unit for the answer is the ratio of grams to moles.

Using Sample Problems

Learning to analyze and solve such problems requires practice and a logical approach. In this section, you will review a process that can help you analyze problems effectively. Most Sample Problems in this book are organized by four basic steps to guide your thinking in how to work out the solution to a problem.

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Analyze

The first step in solving a quantitative word problem is to read the problem carefully at least twice and to analyze the information in it. Note any important descriptive terms that clarify or add meaning to the problem. Identify and list the data given in the problem. Also identify the unknown—the quantity you are asked to find.

Plan

The second step is to develop a plan for solving the problem. The plan should show how the information given is to be used to find the unknown. In the process, reread the problem to make sure you have gathered all the necessary information. It is often helpful to draw a picture that represents the problem. For example, if you were asked to determine the volume of a crystal given its dimensions, you could draw a representation of the crystal and label the dimensions. This drawing would help you visualize the problem.

Decide which conversion factors, mathematical formulas, or chemical principles you will need to solve the problem. Your plan might suggest a single calculation or a series of them involving different conversion factors. Once you understand how you need to proceed, you may wish to sketch out the route you will take, using arrows to point the way from one stage of the solution to the next. Sometimes you will need data that are not actually part of the problem statement. For instance, you'll often use data from the periodic table.

Compute

The third step involves substituting the data and necessary conversion factors into the plan you have developed. At this stage you calculate the answer, cancel units, and round the result to the correct number of significant figures. It is very important to have a plan worked out in step 2 before you start using the calculator. All too often, students start multiplying or dividing values given in the problem before they really understand what they need to do to get an answer.

Evaluate

Examine your answer to determine whether it is reasonable. Use the following methods, when appropriate, to carry out the evaluation.

1. Check to see that the units are correct. If they are not, look over the setup. Are the conversion factors correct?
2. Make an estimate of the expected answer. Use simpler, rounded numbers to do so. Compare the estimate with your actual result. The two should be similar.
3. Check the order of magnitude in your answer. Does it seem reasonable compared with the values given in the problem? If you calculated the density of vegetable oil and got a value of 54.9 g/mL, you would know that something is wrong. Oil floats on water; therefore, its density is less than water, so the value obtained should be less than 1.0 g/mL.
4. Be sure that the answer given for any problem is expressed using the correct number of significant figures.

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Look over the following quantitative Sample Problems. Notice how the four-step approach is used in each, and then apply the approach yourself in solving the practice problems that follow.

SAMPLE PROBLEM 2-6

Calculate the volume of a sample of aluminum that has a mass of 3.057 kg. The density of aluminum is 2.70 g/cm^3.

SOLUTION

1 ANALYZE

Given: mass = 3.057 kg, density = 2.70 g/cm^3
Unknown: volume of aluminum

2 PLAN

The density unit in the problem is g/cm^3, and the mass given in the problem is expressed in kg. Therefore, in addition to using the density equation, you will need a conversion factor representing the relationship between grams and kilograms.

$$1000 \text{ g} = 1 \text{ kg}$$

Also, rearrange the density equation to solve for volume.

$$density = \frac{mass}{volume} \quad \text{or} \quad D = \frac{m}{V}$$

$$V = \frac{m}{D}$$

3 COMPUTE

$$V = \frac{3.057 \text{ kg}}{2.70 \text{ g/cm}^3} \times \frac{1000 \text{ g}}{\text{kg}} = 1132.222 \ldots \text{ cm}^3 \text{ (calculator answer)}$$

The answer should be rounded to three significant figures.

$$V = 1.13 \times 10^3 \text{ cm}^3$$

4 EVALUATE

The unit of volume, cm^3, is correct. An order-of-magnitude estimate would put the answer at over 1000 cm^3.

$$\frac{3}{2} \times 1000$$

The correct number of significant digits is three, to match the number of significant figures in 2.70 g/cm^3.

PRACTICE

1. What is the volume of a sample of helium that has a mass of 1.73×10^{-3} g, given that the density is 0.178 47 g/L?
   Answer 9.69 mL
2. What is the density of a piece of metal that has a mass of 6.25×10^5 g and is 92.5 cm × 47.3 cm × 85.4 cm?
   Answer 1.67 g/cm^3
3. How many millimeters are there in 5.12×10^5 kilometers?
   Answer 5.12×10^{11} mm
4. A clock gains 0.020 second per minute. How many seconds will the clock gain in exactly six months, assuming exactly 30 days per month?
   Answer 5.2×10^3 s

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Direct Proportions

Two quantities are **directly proportional** *to each other if dividing one by the other gives a constant value*. For example, if the masses and volumes of different samples of aluminum are measured, the masses and volumes will be directly proportional to each other. As the masses of the samples increase, their volumes increase at the same rate, as you can see from the data in Table 2-7. Doubling the mass doubles the volume. Halving the mass halves the volume.

When two variables, x and y, are directly proportional to each other, the relationship can be expressed as $y \propto x$, which is read as "y is *proportional* to x." The general equation for a directly proportional relationship between the two variables can also be written as follows.

$$\frac{y}{x} = k$$

The value of k is a constant called the proportionality constant. Written in this form, the equation expresses an important fact about direct proportion: the ratio between the variables remains constant. Note that using the mass and volume values in Table 2-7 gives a mass-volume ratio that is constant (neglecting measurement error). The equation can be rearranged into the following form.

$$y = kx$$

The equation $y = kx$ may look familiar to you. It is the equation for a special case of a straight line. If two variables related in this way are graphed versus one another, a straight line, or linear plot that passes through the origin (0,0), results. The data for aluminum from Table 2-7 are graphed in Figure 2-11. The mass and volume of a pure substance are directly proportional to each other. Consider mass to be y and volume to be x. The constant ratio, k, for the two variables is density. The slope of the line reflects the constant density, or mass-volume ratio, of

TABLE 2-7 *Mass-Volume Data for Aluminum at 20°C*

Mass (g)	Volume (cm^3)	$\frac{m}{V}$ (g/cm^3)
54.4	20.1	2.70
65.7	24.15	2.72
83.5	30.9	2.70
97.2	35.8	2.71
105.7	39.1	2.70

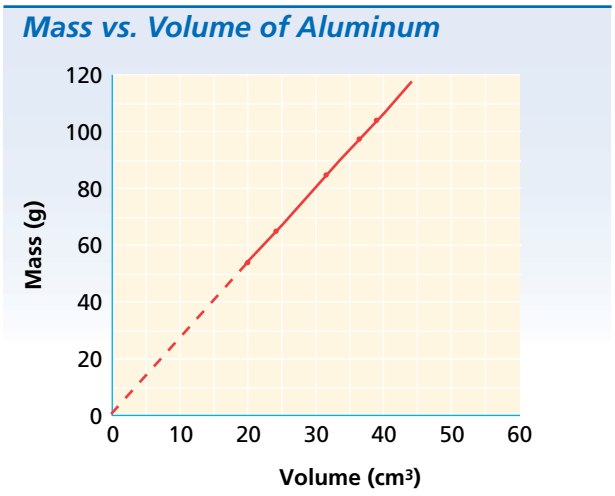

FIGURE 2-11 The graph of mass versus volume shows a relationship of direct proportion. Notice that the line is extrapolated to pass through the origin.

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aluminum, which is 2.70 g/cm^3 at 20°C. Notice also that the plotted line passes through the origin. All directly proportional relationships produce linear graphs that pass through the origin.

Inverse Proportions

Two quantities are **inversely proportional** *to each other if their product is constant*. An example of an inversely proportional relationship is that between speed of travel and the time required to cover a fixed distance. The greater the speed, the less time that is needed to go a certain fixed distance. Doubling the speed cuts the required time in half. Halving the speed doubles the required time.

When two variables, x and y, are inversely proportional to each other, the relationship can be expressed as follows.

$$y \propto \frac{1}{x}$$

This is read "y is *proportional* to 1 divided by x." The general equation for an inversely proportional relationship between the two variables can be written in the following form.

$$xy = k$$

In the equation, k is the proportionality constant. If x increases, y must decrease to keep the product constant.

A graph of variables that are inversely proportional produces a curve called a hyperbola. Such a graph is illustrated in Figure 2-12. When the temperature of the gas is kept constant, the volume (V) of the gas sample decreases as the pressure (P) increases. Look at the data shown in Table 2-8. Note that $P \times V$ gives a reasonably constant value. The graph of this data is shown in Figure 2-12.

TABLE 2-8 *Pressure-Volume Data for Nitrogen at Constant Temperature*

Pressure (kPa)	Volume (cm^3)	$P \times V$
100	500	50 000
150	333	49 500
200	250	50 000
250	200	50 000
300	166	49 800
350	143	50 500
400	125	50 000
450	110	49 500

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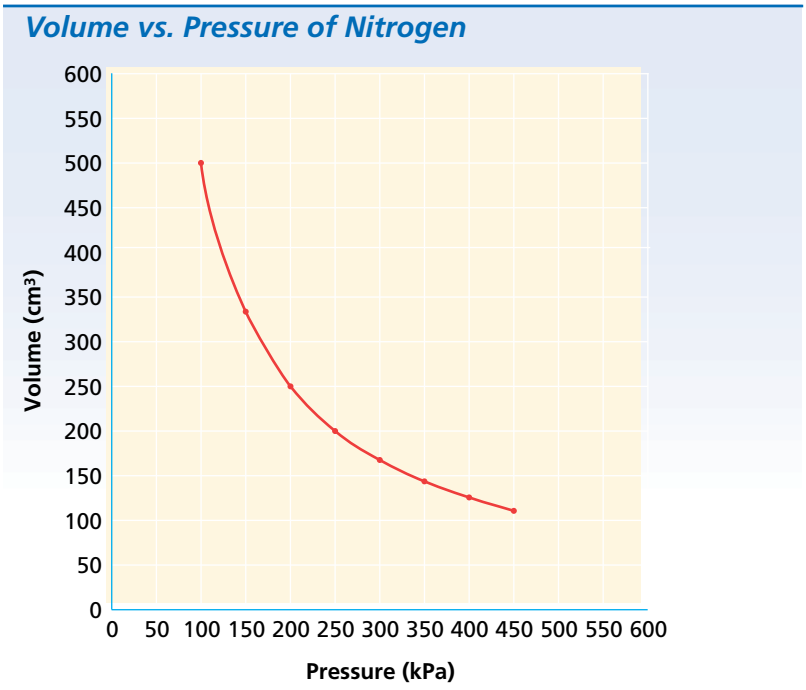

FIGURE 2-12 The graph of volume versus pressure shows an inversely proportional relationship. Note the difference between the shape of this graph and that of the graph in Figure 2-11.

SECTION REVIEW

1. The density of copper is listed as 8.94 g/cm^3. Two students each make three density determinations of samples of the substance. Student A's results are 7.3 g/mL, 9.4 g/mL, and 8.3 g/mL. Student B's results are 8.4 g/cm^3, 8.8 g/cm^3, and 8.0 g/cm^3. Compare the two sets of results in terms of precision and accuracy.
2. How many significant figures are there in each of the following measured values?
   a. 6.002 cm
   b. 0.0020 m
   c. 10.0500 g
   d. 7000 kg
   e. 7000. kg
3. Round 2.6765 to two significant figures.
4. Carry out the following calculations.
   a. 52.13 g + 1.7502 g
   b. 12 m × 6.41 m
   c. $\dfrac{16.25\ \text{g}}{5.1442\ \text{mL}}$
5. Perform the following operations. Express each answer in scientific notation.
   a. $(1.54 \times 10^{-2}\ \text{g}) + (2.86 \times 10^{-1}\ \text{g})$
   b. $(7.023 \times 10^{9}\ \text{g}) - (6.62 \times 10^{7}\ \text{g})$
   c. $(8.99 \times 10^{-4}\ \text{m}) \times (3.57 \times 10^{4}\ \text{m})$
   d. $\dfrac{2.17 \times 10^{-3}\ \text{g}}{5.022 \times 10^{4}\ \text{mL}}$
6. Write the following numbers in scientific notation.
   a. 560 000
   b. 33 400
   c. 0.000 4120
7. A student measures the mass of a beaker filled with corn oil. The mass reading averages 215.6 g. The mass of the beaker is 110.4 g.
   a. What is the mass of the corn oil?
   b. What is the density of the corn oil if its volume is 114 cm^3?
8. Calculate the mass of a sample of gold that occupies 5.0×10^{-3} cm^3. The density of gold is 19.3 g/cm^3.
9. What is the difference between a graph representing data that are directly proportional and a graph of data that are inversely proportional?

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CHAPTER 2 REVIEW

CHAPTER SUMMARY

2-1

- The scientific method is a logical approach to solving problems that lend themselves to investigation.
- The processes of observing, generalizing, theorizing, and testing are aspects of the scientific method.
- A hypothesis is a testable statement that serves as the basis for predictions and further experiments.
- A theory is a broad generalization that explains a body of known facts or phenomena.

Vocabulary

hypothesis (30) scientific method (29) system (29) theory (31)
model (31)

2-2

- The result of nearly every measurement is a number and a unit.
- The SI system of measurement is used in science. It has seven base units: the meter (length), kilogram (mass), second (time), kelvin (temperature), mole (quantity of substance), ampere (electric current), and candela (luminous intensity).
- Weight is a measure of the gravitational pull on matter.
- Derived SI units include the square meter (area) and the cubic meter (volume).
- Density is the ratio of mass to volume.
- Conversion factors are used to convert from one unit to another.

Vocabulary

conversion factor (40) derived unit (36) SI (33) weight (35)
density (38) quantity (33) volume (37)

2-3

- Accuracy refers to the closeness of a measurement to the correct or accepted value. Precision refers to the closeness of values for a set of measurements.
- The measurement average is the sum of a group of measurements divided by the total number of measurements.
- Percent error is the difference between the accepted and the experimental value, divided by the accepted value, then multiplied by 100.
- The significant figures in a number consist of all digits known with certainty plus one final digit, which is uncertain or estimated. A set of logical rules must be followed to determine the number of significant figures in numbers containing zeros.
- After addition or subtraction, the answer should be rounded so that it has no more digits to the right of the decimal point than there are in the measurement with the smallest number of digits to the right of the decimal point. After multiplication or division, the answer should be rounded so that it has no more significant figures than there are in the measurement with the fewest number of significant figures.
- Exact conversion factors are completely certain and do not limit the number of digits in a calculation.
- A number written in scientific notation is of the form $M \times 10^n$, where M is greater than or equal to 1 but less than 10 and n is an integer.
- Two quantities are directly proportional to each other if dividing one by the other gives a constant value. The graphs of variables related in this way are straight lines that pass through the origin.
- Two quantities are inversely proportional to each other if their product has a constant value. The graphs of variables related in this way are hyperbolas.

Vocabulary

accuracy (44) indirectly proportional (56) precision (44) significant figures (46)
directly proportional (55) percent error (45) scientific notation (50)

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REVIEWING CONCEPTS

1. How does quantitative information differ from qualitative information? (2-1)

2. What is a hypothesis? (2-1)

3. a. What is a model in the scientific sense?
b. How does a model differ from a theory? (2-1)

4. Why is it important for a measurement system to have an international standard? (2-2)

5. How does a quantity differ from a unit? Use two examples to explain the difference. (2-2)

6. List the seven SI base units and the quantities they represent. (2-2)

7. What is the numerical equivalent of each of the following SI prefixes?
a. kilo-
b. centi-
c. mega-
d. micro-
e. milli- (2-2)

8. Identify the SI unit that would be most appropriate for expressing the length of the following.
a. width of a gymnasium
b. length of a finger
c. distance between your town and the closest border of the next state
d. length of a bacterial cell (2-2)

9. Identify the SI unit that would be most appropriate for measuring the mass of each of the following objects.
a. table
b. coin
c. a 250 mL beaker (2-2)

10. Explain why the second is not defined by the length of the day. (2-2)

11. a. What is a derived unit?
b. What is the SI derived unit for area? (2-2)

12. a. List two SI derived units for volume.
b. List two non-SI units for volume, and explain how they relate to the cubic centimeter. (2-2)

13. a. Why are the units used to express the densities of gases different from those used to express the densities of solids or liquids?
b. Name two units for density.
c. Why is the temperature at which a density is measured usually specified? (2-2)

14. a. Which of the solids listed in Table 2-4 will float on water?
b. Which of the liquids will sink in milk?

15. a. Define *conversion factor*.
b. Explain how conversion factors are used. (2-2)

16. Contrast accuracy and precision. (2-3)

17. a. Write the equation that is used to calculate percent error.
b. Under what condition will percent error be negative? (2-3)

18. How is the average for a set of values calculated?

19. What is meant by a mass measurement expressed in this form: $4.6\ g \pm 0.2\ g$?

20. Suppose a graduated cylinder were not correctly calibrated. How would this affect the results of a measurement? How would it affect the results of a calculation using this measurement?

21. Round each of the following measurements to the number of significant figures indicated.
a. 67.029 g to three significant figures
b. 0.15 L to one significant figure
c. 52.8005 mg to five significant figures
d. 3.174 97 mol to three significant figures (2-3)

22. State the rules governing the number of significant figures that result from each of the following operations.
a. addition and subtraction
b. multiplication and division (2-3)

23. What is the general form for writing numbers in scientific notation? (2-3)

24. a. State the general equation for quantities that are directly proportional.
b. For two directly proportional quantities, what happens to one variable when the other increases? (2-3)

25. a. State the general equation for quantities that are inversely proportional.
b. For two inversely proportional quantities, what happens to one variable when the other increases? (2-3)

26. Arrange in proper order the following four basic steps in working out the solution to a problem: compute, plan, evaluate, analyze. (2-3)

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PROBLEMS

Volume and Density

27. What is the volume, in cubic meters, of a rectangular solid that is 0.25 m long, 6.1 m wide, and 4.9 m high?

28. Find the density of a material, given that a 5.03 g sample occupies 3.24 mL. (Hint: See Sample Problem 2-1.)

29. What is the mass of a sample of material that has a volume of 55.1 cm^3 and a density of 6.72 g/cm^3?

30. A sample of a substance that has a density of 0.824 g/mL has a mass of 0.451 g. Calculate the volume of the sample.

Conversion Factors

31. How many grams are there in 882 μg? (Hint: See Sample Problem 2-2.)

32. Calculate the number of mL in 0.603 L.

33. The density of gold is 19.3 g/cm^3.
a. What is the volume, in cm^3, of a sample of gold with mass 0.715 kg?
b. If this sample of gold is a cube, how long is each edge in cm?

34. a. Find the number of km in 92.25 m.
b. Convert the answer in km to cm.

Percent Error

35. A student measures the mass of a sample as 9.67 g. Calculate the percent error, given that the correct mass is 9.82 g. (Hint: See Sample Problem 2-3.)

36. A handbook gives the density of calcium as 1.54 g/cm^3. What is the percent error of a density calculation of 1.25 g/cm^3 based on lab measurements?

37. What is the percent error of a length measurement of 0.229 cm if the correct value is 0.225 cm?

Significant Figures

38. How many significant figures are there in each of the following measurements? (Hint: See Sample Problem 2-4.)
a. 0.4004 mL
b. 6000 g
c. 1.000 30 km
d. 400. mm

39. Calculate the sum of 6.078 g and 0.3329 g.

40. Subtract 7.11 cm from 8.2 cm. (Hint: See Sample Problem 2-5.)

41. What is the product of 0.8102 m and 3.44 m?

42. Divide 94.20 g by 3.167 22 mL.

Scientific Notation

43. Write the following numbers in scientific notation.
a. 0.000 673 0
b. 50 000.0
c. 0.000 003 010

44. The following numbers are in scientific notation. Write them in ordinary notation.
a. 7.050×10^{-3} g
b. $4.000\ 05 \times 10^{7}$ mg
c. $2.350\ 0 \times 10^{4}$ mL

45. Perform the following operation. Express the answer in scientific notation and with the correct number of significant figures.

$$\frac{6.124\ 33 \times 10^{6}\ m^3}{7.15 \times 10^{-3}\ m}$$

46. A sample of a certain material has a mass of 2.03×10^{-3} g. Calculate the volume of the sample, given that the density is 9.133×10^{-1} g/cm^3. Use the four-step method in solving the problem. (Hint: See Sample Problem 2-6.)

MIXED REVIEW

47. A man finds that he has a mass of 100.6 kg. He goes on a diet, and several months later he finds that he has a mass of 96.4 kg. Express each number in scientific notation, and calculate the number of kilograms the man has lost by dieting.

48. A large office building is 1.07×10^{2} m long, 31 m wide, and 4.25×10^{2} m high. What is its volume?

49. An object is found to have a mass of 57.6 g. Find the object's density, given that its volume is 40.25 cm^3.

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50. A student measures the mass of some sucrose as 0.947 mg. Convert that quantity to grams and to kilograms.

51. A student calculates the density of iron as 6.80 g/cm^3 using lab data for mass and volume. A handbook reveals that the correct value is 7.86 g/cm^3. What is the percent error?

HANDBOOK SEARCH

52. Find the table of properties for Group 1 elements in the *Elements Handbook,* pages 726–783. Calculate the volume of a single atom of each element listed in the table using the equation for the volume of a sphere.

$$\frac{4}{3}\pi r^3$$

53. Use the radius of a sodium atom from the *Elements Handbook* to calculate the number of sodium atoms in a row 5.00 cm long. Assume that each sodium atom touches its two neighbors.

54. a. A block of sodium with measurements 3.00 cm × 5.00 cm × 5.00 cm has a measured mass of 75.5 g. Calculate the density of sodium.

b. Compare your calculated density with the value in the properties table for Group 1 elements. Calculate the percent error for your density determination.

RESEARCH & WRITING

55. Find out how the metric system, which was once a standard for measurement, differs from SI. Why was it necessary to change to SI?

56. Find out what ISO 9000 standards are. How do they affect industry on an international level?

ALTERNATIVE ASSESSMENT

57. **Performance** Obtain three metal samples from your teacher. Determine the mass and volume of each sample. Calculate the density of each metal from your measurement data. (Hint: Consider using the water displacement technique to measure the volume of your samples.)

58. Using the data from the Nutrition Facts label below, answer the following.

a. Use the data given on the label for grams of fat and Calories from fat to construct a conversion factor with the units Calories per gram.

b. Calculate the mass in kilograms of 20 servings of the food.

c. Calculate the mass of protein in micrograms for one serving of the food.

d. What is the correct number of significant figures for the answer in item a? Why?

Nutrition Facts

Serving Size ¾ cup (30g)
Servings Per Container About 14

Amount Per Serving	Corn Crunch	with ½ cup skim milk
Calories	120	160
Calories from Fat	15	20
	% Daily Value**	
Total Fat 2g*	**3**%	**3**%
Saturated Fat 0g	**0**%	**0**%
Cholesterol 0mg	**0**%	**1**%
Sodium 160mg	**7**%	**9**%
Potassium 65mg	**2**%	**8**%
Total Carbohydrate 25g	**8**%	**10**%
Dietary Fiber 3g		
Sugars 3g		
Other Carbohydrate 11g		
Protein 2g		

*Amount in Cereal. A serving of cereal plus skim milk provides 2g fat, less 5mg cholesterol, 220mg sodium, 270mg potassium, 31g carbohydrate (19g sugars) and 6g protein.

**Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs:

	Calories	2,000	2,500
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400mg	2,400mg
Potassium		3,500mg	3,500mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

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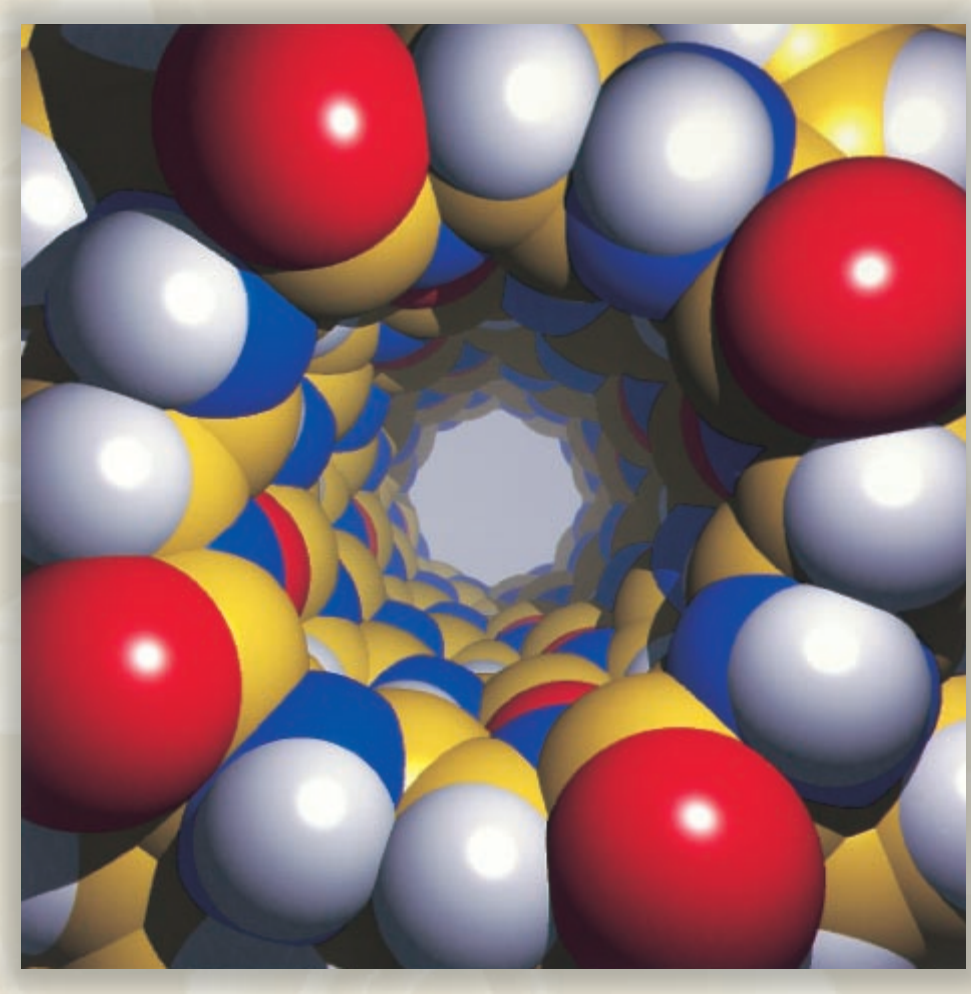
CHAPTER 3

Atoms: The Building Blocks of Matter



An atom is the smallest particle of an element that retains the chemical properties of that element.

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The Atom: From Philosophical Idea to Scientific Theory

SECTION 3-1

Objectives

- Explain the law of conservation of mass, the law of definite proportions, and the law of multiple proportions.
- Summarize the five essential points of Dalton's atomic theory.
- Explain the relationship between Dalton's atomic theory and the law of conservation of mass, the law of definite proportions, and the law of multiple proportions.

When you crush a lump of sugar, you can see that it is made up of many smaller particles of sugar. You may grind these particles into a very fine powder, but each tiny piece is still sugar. Now suppose you dissolve the sugar in water. The tiny particles seem to disappear completely. Even if you look at the sugar-water solution through a powerful microscope, you cannot see any sugar particles. Yet if you were to taste the solution, you'd know that the sugar is still there. Observations like these led early philosophers to ponder the fundamental nature of matter. Is it continuous and infinitely divisible, or is it divisible only until a basic, invisible particle that cannot be divided further is reached?

The particle theory of matter was supported as early as 400 B.C. by certain Greek thinkers, such as Democritus. He called nature's basic particle an *atom,* based on the Greek word meaning "indivisible." Aristotle was part of the generation that succeeded Democritus. His ideas had a lasting impact on Western civilization, and he did not believe in atoms. He thought that all matter was continuous, and his opinion was accepted for nearly 2000 years. Neither the view of Aristotle nor that of Democritus was supported by experimental evidence, so each remained speculation until the eighteenth century. Then scientists began to gather evidence favoring the atomic theory of matter.

Foundations of Atomic Theory

Virtually all chemists in the late 1700s accepted the modern definition of an element as a substance that cannot be further broken down by ordinary chemical means. It was also clear that elements combine to form compounds that have different physical and chemical properties than those of the elements that form them. There was great controversy, however, as to whether elements always combine in the same ratio when forming a particular compound.

The transformation of a substance or substances into one or more new substances is known as a *chemical reaction*. In the 1790s, the study of matter was revolutionized by a new emphasis on the quantitative

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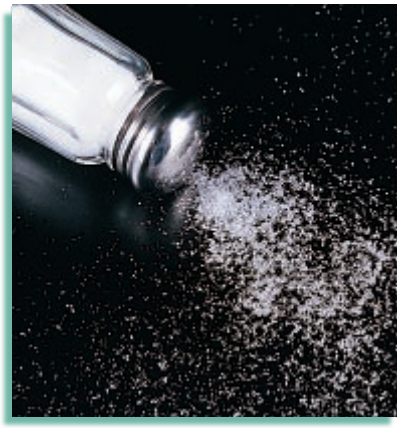

FIGURE 3-1 Each of the salt crystals shown here contains exactly 39.34% sodium and 60.66% chlorine by mass.

analysis of chemical reactions. Aided by improved balances, investigators began to accurately measure the masses of the elements and compounds they were studying. This lead to the discovery of several basic laws. One of these laws was the **law of conservation of mass,** *which states that mass is neither destroyed nor created during ordinary chemical reactions or physical changes*. This discovery was soon followed by the assertion that, regardless of where or how a pure chemical compound is prepared, it is composed of a fixed proportion of elements. For example, sodium chloride, also known as ordinary table salt, *always* consists of 39.34% by mass of the element sodium, Na, and 60.66% by mass of the element chlorine, Cl. *The fact that a chemical compound contains the same elements in exactly the same proportions by mass regardless of the size of the sample or source of the compound is known as the* **law of definite proportions.**

It was also known that two elements sometimes combine to form more than one compound. For example, the elements carbon and oxygen form two compounds, carbon dioxide and carbon monoxide. Consider samples of each of these compounds, each containing 1.0 g of carbon. In carbon dioxide, 2.66 g of oxygen combine with 1.0 g of carbon. In carbon monoxide, 1.33 g of oxygen combine with 1.0 g of carbon. The ratio of the masses of oxygen in these two compounds is exactly 2.66 to 1.33, or 2 to 1. This illustrates the **law of multiple proportions:** *If two or more different compounds are composed of the same two elements, then the ratio of the masses of the second element combined with a certain mass of the first element is always a ratio of small whole numbers.*

Dalton's Atomic Theory

In 1808, an English schoolteacher named John Dalton proposed an explanation for the law of conservation of mass, the law of definite proportions, and the law of multiple proportions. He reasoned that elements were composed of atoms and that only whole numbers of atoms can combine to form compounds. His theory can be summed up by the following statements.

1. All matter is composed of extremely small particles called atoms.
2. Atoms of a given element are identical in size, mass, and other properties; atoms of different elements differ in size, mass, and other properties.
3. Atoms cannot be subdivided, created, or destroyed.
4. Atoms of different elements combine in simple whole-number ratios to form chemical compounds.
5. In chemical reactions, atoms are combined, separated, or rearranged.

According to Dalton's atomic theory, the law of conservation of mass is explained by the fact that chemical reactions involve merely the combination, separation, or rearrangement of atoms and that during these processes atoms are not subdivided, created, or destroyed. This

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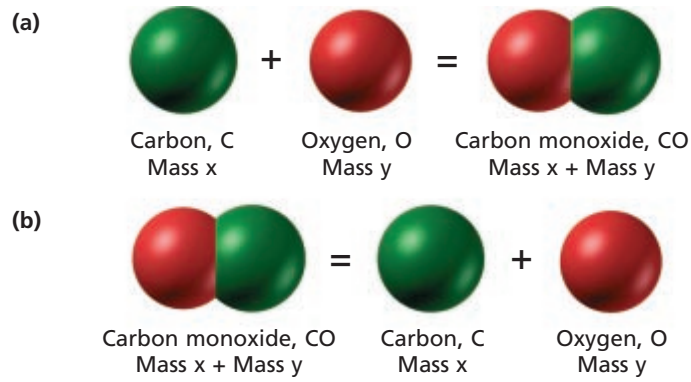

FIGURE 3-2 (a) An atom of carbon, C, and an atom of oxygen, O, can combine chemically to form a molecule of carbon monoxide, CO. The mass of the CO molecule is equal to the mass of the C atom plus the mass of the O atom. (b) The reverse holds true in a reaction in which a CO molecule is broken down into its elements.

idea is illustrated in Figure 3-2 for the formation of carbon monoxide from carbon and oxygen.

The law of definite proportions, on the other hand, results from the fact that a given chemical compound is always composed of the same combination of atoms (see Figure 3-3). As for the law of multiple proportions, in the case of the carbon oxides, the 2-to-1 ratio of oxygen masses results because carbon dioxide always contains twice as many atoms of oxygen (per atom of carbon) as does carbon monoxide. This can also be seen in Figure 3-3.

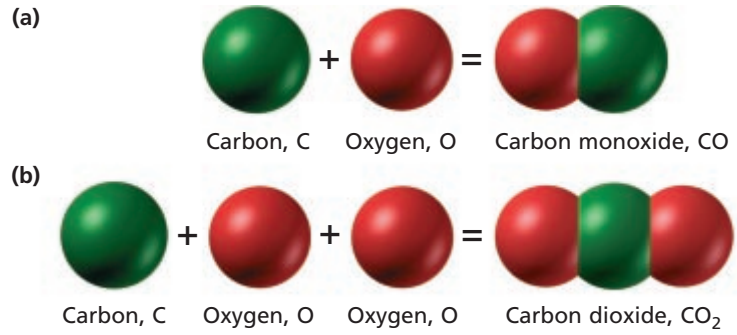

FIGURE 3-3 (a) CO molecules are always composed of one C atom and one O atom. (b) CO_2 molecules are always composed of one C atom and two O atoms. Note that a molecule of carbon dioxide contains twice as many oxygen atoms as does a molecule of carbon monoxide.

Modern Atomic Theory

By relating atoms to the measurable property of mass, Dalton turned Democritus's *idea* into a *scientific theory* that could be tested by experiment. But not all aspects of Dalton's atomic theory have proven to be correct. For example, today we know that atoms are divisible into even smaller particles (although the law of conservation of mass still holds true for chemical reactions). And, as you will see in Section 3-3, we know that a given element can have atoms with different masses. Atomic theory has not been discarded, however. Instead, it has been modified to explain the new observations. The important concepts that (1) all matter is composed of atoms and that (2) atoms of any one element differ in properties from atoms of another element remain unchanged.

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CHEMICAL COMMENTARY

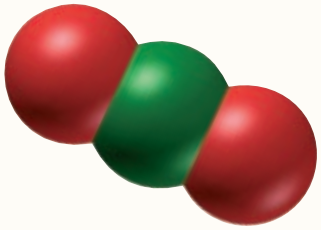
Travels with C

From "Travels with C" by Primo Levi in *Creation to Chaos*

It was to carbon, the element of life, that my first literary dream was turned—and now I want to tell the story of a single atom of carbon.

My fictional character lies, for hundreds of millions of years, bound to three atoms of oxygen and one of calcium, in the form of limestone. (It already has behind it a very long cosmic history, but that we shall ignore.) Time does not exist for it, or exists only in the form of sluggish daily or seasonal variations in temperature. Its existence, whose monotony cannot be conceived of without horror, is an alternation of hots and colds.

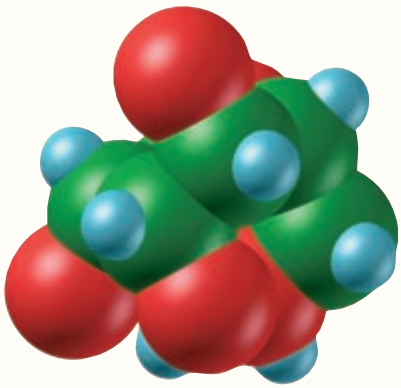
The limestone ledge of which the atom forms a part lies within reach of man and his pickax. At any moment—which I, as narrator, decide out of pure caprice to be the year of 1840—a blow of the pickax detached the limestone and sent it on its way to the lime furnace, where it was plunged into the world of things that change. The atom of carbon was roasted until it separated from the limestone's calcium, which remained, so to speak, with its feet on the ground and went on to meet a less brilliant destiny. Still clinging firmly to two of its three companions, our fictional character issued from the chimney and rode the path of the air. Its story, which once was immobile, now took wing.



Accompanied by two oxygen atoms (red), the carbon atom (green) took to the air.

The atom was caught by the wind, flung down onto the earth, lifted ten kilometers high. It was breathed in by a falcon, but did not penetrate the bird's rich blood and was exhaled. It dissolved three times in the sea, once in the water of a cascading torrent, and again was expelled. It traveled with the wind for eight years—now high, now low, on the sea and among the clouds, over forests, deserts and limitless expanses of ice. Finally, it stumbled into capture and the organic adventure.

The year was 1848. The atom of carbon, accompanied by its two satellites of oxygen, which maintained it in a gaseous state, was borne by the wind along a row of vines. It had the good fortune to brush against a leaf, penetrate it, and be nailed there by a ray of the sun. On entering the leaf, it collided with other innumerable molecules of nitrogen and oxygen. It adhered to a large and complicated molecule that activated it, and simultaneously it received the decisive message from the sky, in the flashing form of a packet of solar light: in an instant, like an insect caught by a spider, the carbon atom was separated from its oxygen, combined with hydrogen, and finally inserted in a chain of life. All this happened swiftly, in silence, at the temperature and pressure of the atmosphere.



Once inside the leaf, the carbon atom joined other carbon atoms (green), as well as hydrogen (blue) and oxygen (red) atoms, to form this molecule essential to life.

Reading for Meaning

Name the various compounds that the carbon atom was a component of during the course of Levi's story.

Read Further

As a component of one particular compound, Levi's carbon atom is breathed in and exhaled by a falcon. Why was it unlikely for the carbon atom to have been taken into the bird's bloodstream?

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Quick LAB

Constructing a Model

Wear Safety Goggles and an Apron.

Materials

- can covered by a sock sealed with tape
- one or more objects that fit in the container
- metric ruler
- balance

Question

How can you construct a model of an unknown object by (1) making inferences about an object that is in a closed container and (2) touching the object without seeing it?

Procedure

1. Your teacher will provide you with a can that is covered by a sock sealed with tape. Without unsealing the container, try to determine the number of objects inside the can as well as the mass, shape, size, composition, and texture of each. To do this, you may carefully tilt or shake the can. Record your observations in a data table.
2. Remove the tape from the top of the sock. Do *not* look inside the can. Put one hand through the opening, and make the same observations as in step 1 by handling the objects. To make more-accurate estimations, practice estimating the sizes and masses of some known objects outside the can. Then compare your estimates of these objects with actual measurements using a metric ruler and a balance.

Discussion

1. Scientists often use more than one method to gather data. How was this illustrated in the investigation?
2. Of the observations you made, which were qualitative and which were quantitative?
3. Using the data you gathered, draw a model of the unknown object(s) and write a brief summary of your conclusions.

SECTION REVIEW

1. Describe the major contributions of each of the following to the modern theory of the atom:
   a. Democritus
   b. John Dalton
2. List the five essential points of Dalton's atomic theory.
3. What chemical laws can be explained on the basis of Dalton's theory?

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SECTION 3-2

OBJECTIVES

- Summarize the observed properties of cathode rays that led to the discovery of the electron.
- Summarize the experiment carried out by Rutherford and his co-workers that led to the discovery of the nucleus.
- List the properties of protons, neutrons, and electrons.
- Define *atom.*

The Structure of the Atom

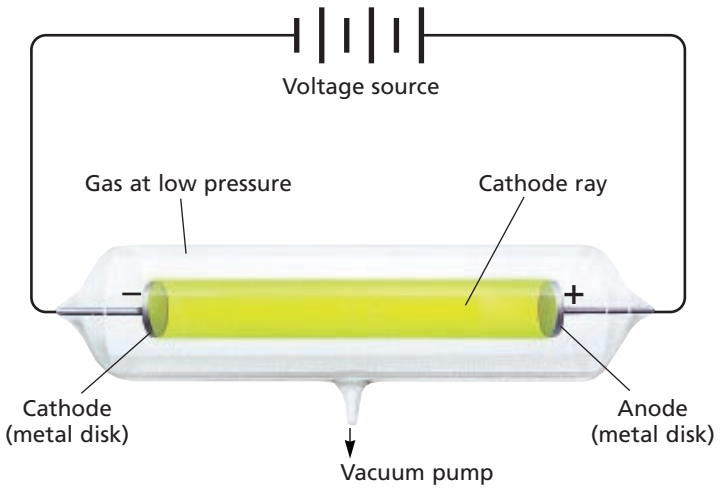
Although John Dalton thought atoms were indivisible, investigators in the late 1800s proved otherwise. As scientific advances allowed a deeper exploration of matter, it became clear that atoms are actually composed of several basic types of smaller particles and that the number and arrangement of these particles within an atom determine that atom's chemical properties. Today we define an **atom** *as the smallest particle of an element that retains the chemical properties of that element.*

All atoms consist of two regions. The *nucleus* is a very small region located near the center of an atom. In every atom the nucleus contains at least one positively charged particle called a *proton* and usually one or more neutral particles called *neutrons.* Surrounding the nucleus is a region occupied by negatively charged particles called *electrons.* This region is very large compared with the size of the nucleus. Protons, neutrons, and electrons are often referred to as *subatomic particles*.

Discovery of the Electron

The first discovery of a subatomic particle resulted from investigations into the relationship between electricity and matter. In the late 1800s, many experiments were performed in which electric current was passed through various gases at low pressures. (Gases at atmospheric pressure don't conduct electricity well.) These experiments were carried out in glass tubes like the one shown in Figure 3-4. Such tubes are known as *cathode-ray tubes*.

FIGURE 3-4 A simple cathode-ray tube. Particles pass through the tube from the *cathode,* the metal disk connected to the negative terminal of the voltage source, to the *anode,* the metal disk connected to the positive terminal.



Cathode Rays and Electrons

Investigators noticed that when current was passed through a cathode-ray tube, the surface of the tube directly opposite the cathode glowed. They hypothesized that the glow was caused by a stream of particles, which they called a cathode ray. The ray traveled from the cathode to the anode when current was passed through the tube. Experiments devised to test

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this hypothesis revealed the following observations.

1. An object placed between the cathode and the opposite end of the tube cast a shadow on the glass.
2. A paddle wheel placed on rails between the electrodes rolled along the rails from the cathode toward the anode (see Figure 3-5).

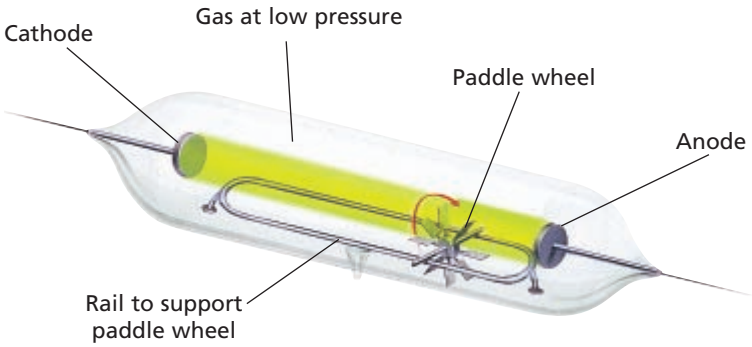

FIGURE 3-5 A paddle wheel placed in the path of the cathode ray moves away from the cathode and toward the anode. The movement of the wheel led scientists to conclude that cathode rays have mass.

These facts supported the existence of a cathode ray. Furthermore, the paddle-wheel experiment showed that a cathode ray had sufficient mass to set the wheel in motion.

Additional experiments provided more information.

3. Cathode rays were deflected by a magnetic field in the same manner as a wire carrying electric current, which was known to have a negative charge.
4. The rays were deflected away from a negatively charged object.

These observations led to the hypothesis that the particles that compose cathode rays are negatively charged. This hypothesis was strongly supported by a series of experiments carried out in 1897 by the English physicist Joseph John Thomson. In one investigation, he was able to measure the ratio of the charge of cathode-ray particles to their mass. He found that this ratio was always the same, regardless of the metal used to make the cathode or the nature of the gas inside the cathode-ray tube. Thomson concluded that all cathode rays are composed of identical negatively charged particles, which were later named electrons.

Charge and Mass of the Electron

Thomson's experiment revealed that the electron has a very large charge for its tiny mass. In 1909, experiments conducted by the American physicist Robert A. Millikan showed that the mass of the electron is in fact about one two-thousandth the mass of the simplest type of hydrogen atom, which is the smallest atom known. More-accurate experiments conducted since then indicate that the electron has a mass of 9.109×10^{-31} kg, or 1/1837 the mass of the simplest type of hydrogen atom.

Millikan's experiments also confirmed that the electron carries a negative electric charge. And because cathode rays have identical properties regardless of the element used to produce them, it was concluded that electrons are present in atoms of all elements. Thus, cathode-ray experiments provided evidence that atoms are divisible and that one of the atom's basic constituents is the negatively charged electron.

Based on what was learned about electrons, two other inferences were made about atomic structure.

1. Because atoms are electrically neutral, they must contain a positive charge to balance the negative electrons.
2. Because electrons have so much less mass than atoms, atoms must contain other particles that account for most of their mass.

CHEMISTRY INTERACTIVE TUTOR
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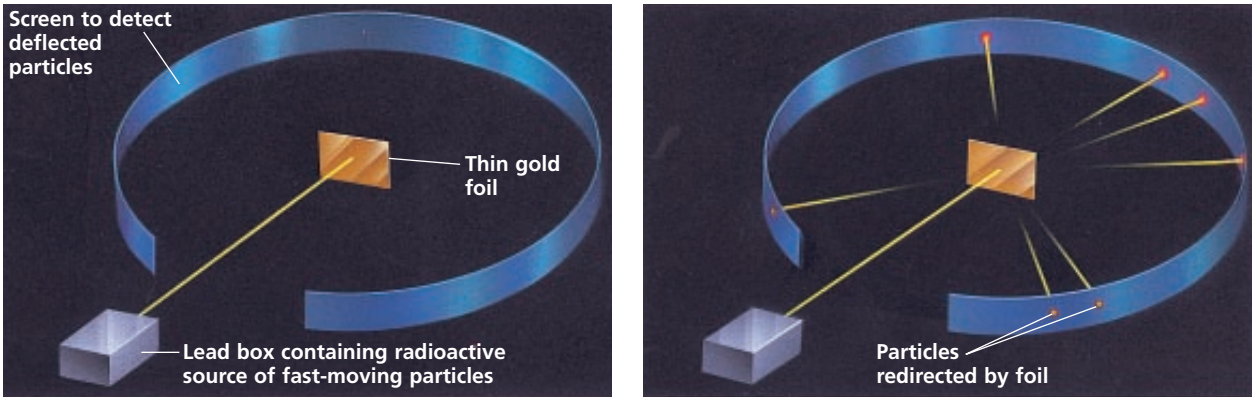
Discovery of the Atomic Nucleus

More detail of the atom's structure was provided in 1911 by New Zealander Ernest Rutherford and his associates Hans Geiger and Ernest Marsden. The scientists bombarded a thin, gold foil with fast-moving *alpha particles,* which are positively charged particles with about four times the mass of a hydrogen atom. Geiger and Marsden assumed that mass and charge were uniformly distributed throughout the atoms of the gold foil. So they expected the alpha particles to pass through with only a slight deflection. And for the vast majority of the particles, this was the case. However, when the scientists checked for the possibility of wide-angle deflections, they were shocked to find that roughly 1 in 8000 of the alpha particles had actually been redirected back toward the source (see Figure 3-6). As Rutherford later exclaimed, it was "as if you had fired a 15-inch [artillery] shell at a piece of tissue paper and it came back and hit you."

After thinking about the startling result for two years, Rutherford finally came up with an explanation. He reasoned that the rebounded alpha particles must have experienced some powerful force within the atom. And he figured that the source of this force must occupy a very small amount of space because so few of the total number of alpha particles had been affected by it. He concluded that the force must be caused by a very densely packed bundle of matter with a positive electric charge. Rutherford called this positive bundle of matter the nucleus (see Figure 3-7).

Rutherford had discovered that the volume of a nucleus was very small compared with the total volume of an atom. In fact, if the nucleus were the size of a marble, then the size of the atom would be about the size of a football field. But where were the electrons? Although he had no supporting evidence, Rutherford suggested that the electrons surrounded the positively charged nucleus like planets around the sun. He could not explain, however, what kept the electrons in motion around the nucleus.

FIGURE 3-6 (a) Geiger and Marsden bombarded a thin piece of gold foil with a narrow beam of alpha particles. (b) Some of the particles were redirected by the gold foil back toward their source.


Screen to detect deflected particles
Thin gold foil
Lead box containing radioactive source of fast-moving particles
Particles redirected by foil

(a) (b)

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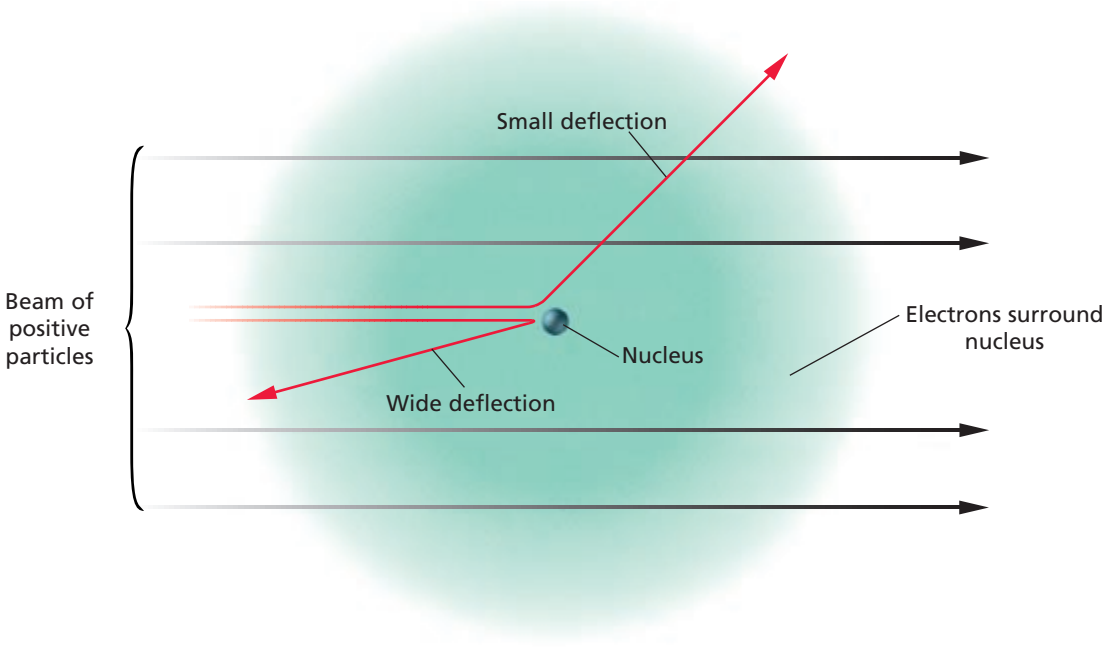

FIGURE 3-7 Rutherford reasoned that each atom in the gold foil contained a small, dense, positively charged nucleus surrounded by electrons. A small number of the alpha particles directed toward the foil were deflected by the tiny nucleus (red arrows). Most of the particles passed through undisturbed (black arrows).

Composition of the Atomic Nucleus

Except for the nucleus of the simplest type of hydrogen atom (discussed in the next section), all atomic nuclei are made of two kinds of particles, protons and neutrons. A proton has a positive charge equal in magnitude to the negative charge of an electron. Atoms are electrically neutral because they contain equal numbers of protons and electrons. A neutron is electrically neutral.

The simplest hydrogen atom consists of a single-proton nucleus with a single electron moving about it. A proton has a mass of 1.673×10^{-27} kg, which is 1836 times greater than the mass of an electron and 1836/1837, or virtually all, of the mass of the simplest hydrogen atom. All atoms besides the simplest hydrogen atom also contain neutrons. The mass of a neutron is 1.675×10^{-27} kg—slightly larger than that of a proton.

The nuclei of atoms of different elements differ in the number of protons they contain and therefore in the amount of positive charge they possess. Thus, the number of protons in an atom's nucleus determines that atom's identity. Physicists have identified other subatomic particles, but particles other than electrons, protons, and neutrons have little effect on the chemical properties of matter. Table 3-1 on page 74 summarizes the properties of electrons, protons, and neutrons.

Forces in the Nucleus

Generally, particles that have the same electric charge repel one another. Therefore, we would expect a nucleus with more than one proton to be unstable. However, when two protons are extremely close to each other, there is a strong attraction between them. In fact, more than 100

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TABLE 3-1 *Properties of Subatomic Particles*

Particle	Symbols	Relative electric charge	Mass number	Relative mass (amu*)	Actual mass (kg)
Electron	$e^-, {}^{0}_{-1}e$	–1	0	0.000 5486	9.109×10^{-31}
Proton	$p^+, {}^{1}_{1}\mathrm{H}$	+1	1	1.007 276	1.673×10^{-27}
Neutron	$n^\circ, {}^{1}_{0}n$	0	1	1.008 665	1.675×10^{-27}

*1 amu (atomic mass unit) = $1.660\,540 \times 10^{-27}$ kg (see page 78)

protons can exist close together in a nucleus. A similar attraction exists when neutrons are very close to each other, or when protons and neutrons are very close together. *These short-range proton-neutron, proton-proton, and neutron-neutron forces hold the nuclear particles together and are referred to as* **nuclear forces.**

The Sizes of Atoms

It is convenient to think of the region occupied by the electrons as an electron cloud—a cloud of negative charge. The radius of an atom is the distance from the center of the nucleus to the outer portion of this electron cloud. Because atomic radii are so small, they are expressed using a unit that is more convenient for the sizes of atoms. This unit is the picometer. The abbreviation for the picometer is pm ($1\ \mathrm{pm} = 10^{-12}\ \mathrm{m} = 10^{-10}\ \mathrm{cm}$). To get an idea of how small a picometer is, consider that 1 cm is the same fractional part of 10^3 km (about 600 mi) as 100 pm is of 1 cm. Atomic radii range from about 40 to 270 pm. By contrast, the nuclei of atoms have much smaller radii, about 0.001 pm. Nuclei also have incredibly high densities, about 2×10^8 metric tons/cm^3.

SECTION REVIEW

1. Define each of the following:
   a. atom
   b. electron
   c. nucleus
   d. proton
   e. neutron
2. Describe one conclusion made by each of the following scientists that led to the development of the current atomic theory:
   a. Thomson
   b. Millikan
   c. Rutherford
3. Compare and contrast the three types of subatomic particles in terms of location in the atom, mass, and relative charge.
4. Why is the cathode-ray tube in Figure 3-4 connected to a vacuum pump?
5. Label the charge on the following in a cathode-ray tube. State the reasons for your answers.
   a. anode
   b. cathode

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Counting Atoms

SECTION 3-3

Objectives

- Explain what isotopes are.
- Define *atomic number* and *mass number,* and describe how they apply to isotopes.
- Given the identity of a nuclide, determine its number of protons, neutrons, and electrons.
- Define *mole* in terms of Avogadro's number, and define *molar mass.*
- Solve problems involving mass in grams, amount in moles, and number of atoms of an element.

Consider neon, Ne, the gas used in many illuminated signs. Neon is a minor component of the atmosphere. In fact, dry air contains only about 0.002% neon. And yet there are about 5×10^{17} atoms of neon present in each breath you inhale. In most experiments, atoms are much too small to be measured individually. Chemists can analyze atoms quantitatively, however, by knowing fundamental properties of the atoms of each element. In this section you will be introduced to some of the basic properties of atoms. You will then discover how to use this information to count the number of atoms of an element in a sample with a known mass. You will also become familiar with the *mole,* a special unit used by chemists to express amounts of particles, such as atoms and molecules.

Atomic Number

All atoms are composed of the same basic particles. Yet all atoms are not the same. Atoms of different elements have different numbers of protons. Atoms of the same element all have the same number of protons. *The* **atomic number** *(Z) of an element is the number of protons in the nucleus of each atom of that element.*

Turn to the inside back cover of this textbook. In the periodic table shown, an element's atomic number is indicated above its symbol. Notice that the elements are placed in order of increasing atomic number. At the top left of the table is hydrogen, H, which has atomic number 1. Atoms of the element hydrogen have one proton in the nucleus. Next in order is helium, He, which has two protons in each nucleus. Lithium, Li, has three protons; beryllium, Be, has four protons; and so on.

The atomic number identifies an element. If you want to know which element has atomic number 47, for example, look at the periodic table. You can see that it is silver, Ag. All silver atoms contain 47 protons in their nuclei. Because atoms are neutral, we know from the atomic number that all silver atoms must also contain 47 electrons.

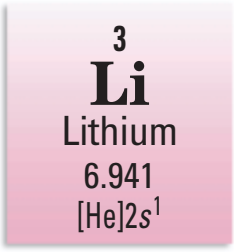

FIGURE 3-8 The atomic number in this periodic-table entry reveals that an atom of lithium has three protons in its nucleus.

Isotopes

The simplest atoms are those of hydrogen. All hydrogen atoms contain only one proton. However, like many naturally occurring elements, hydrogen atoms can contain different numbers of neutrons.

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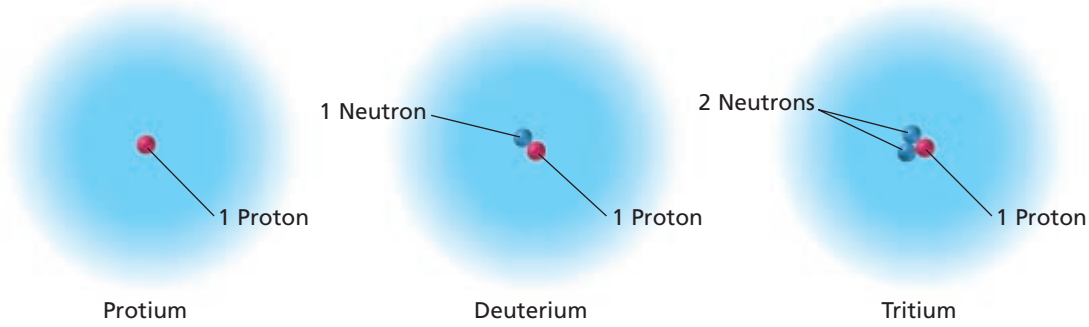

FIGURE 3-9 The nuclei of different isotopes of the same element have the same number of protons but different numbers of neutrons. This is illustrated above by the three isotopes of hydrogen.

Three types of hydrogen atoms are known. The most common type of hydrogen is sometimes called *protium.* It accounts for 99.985% of the hydrogen atoms found on Earth. The nucleus of a protium atom consists of one proton only, and it has one electron moving about it. There are two other known forms of hydrogen. One is called *deuterium,* which accounts for 0.015% of Earth's hydrogen atoms. Each deuterium atom has a nucleus containing one proton and one neutron. The third form of hydrogen is known as *tritium,* which is radioactive. It exists in very small amounts in nature, but it can be prepared artificially. Each tritium atom contains one proton, two neutrons, and one electron.

Protium, deuterium, and tritium are isotopes of hydrogen. **Isotopes** *are atoms of the same element that have different masses.* The isotopes of a particular element all have the same number of protons and electrons but different numbers of neutrons. In all three isotopes of hydrogen, the positive charge of the single proton is balanced by the negative charge of the electron. Most of the elements consist of mixtures of isotopes. Tin has 10 stable isotopes, for example, the most of any element.

Mass Number

Identifying an isotope requires knowing both the name or atomic number of the element and the mass of the isotope. *The* **mass number** *is the total number of protons and neutrons in the nucleus of an isotope.* The three isotopes of hydrogen described earlier have mass numbers 1, 2, and 3, as shown in Table 3-2.

TABLE 3-2 *Mass Numbers of Hydrogen Isotopes*

	Atomic number (number of protons)	Number of neutrons	Mass number
Protium	1	0	1 + 0 = 1
Deuterium	1	1	1 + 1 = 2
Tritium	1	2	1 + 2 = 3

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Designating Isotopes

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The isotopes of hydrogen are unusual in that they have distinct names. Isotopes are usually identified by specifying their mass number. There are two methods for specifying isotopes. In the first method, the mass number is written with a hyphen after the name of the element. Tritium, for example, is written as hydrogen-3. We will refer to this method as *hyphen notation.* The uranium isotope used as fuel for nuclear power plants has a mass number of 235 and is therefore known as uranium-235. The second method shows the composition of a nucleus as the isotope's *nuclear symbol*. For example, uranium-235 is written as $^{235}_{92}U$. The superscript indicates the mass number and the subscript indicates the atomic number. The number of neutrons is found by subtracting the atomic number from the mass number.

mass number – atomic number = number of neutrons
235 (protons + neutrons) – 92 protons = 143 neutrons

Thus, a uranium-235 nucleus contains 92 protons and 143 neutrons.

Table 3-3 gives the names, symbols, and compositions of the isotopes of hydrogen and helium. **Nuclide** *is a general term for any isotope of any element.* We could say that Table 3-3 lists the compositions of five different nuclides.

TABLE 3-3 *Isotopes of Hydrogen and Helium*

Isotope	Nuclear symbol	Number of protons	Number of electrons	Number of neutrons
Hydrogen-1 (protium)	$^{1}_{1}H$	1	1	0
Hydrogen-2 (deuterium)	$^{2}_{1}H$	1	1	1
Hydrogen-3 (tritium)	$^{3}_{1}H$	1	1	2
Helium-3	$^{3}_{2}He$	2	2	1
Helium-4	$^{4}_{2}He$	2	2	2

SAMPLE PROBLEM 3-1

How many protons, electrons, and neutrons are there in an atom of chlorine-37?

SOLUTION

1 ***ANALYZE***

Given: name and mass number of chlorine-37
Unknown: numbers of protons, electrons, and neutrons

2 ***PLAN***

atomic number = number of protons = number of electrons
mass number = number of neutrons + number of protons

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3 COMPUTE

The mass number of chlorine-37 is 37. Consulting the periodic table reveals that chlorine's atomic number is 17. The number of neutrons can be found by subtracting the atomic number from the mass number.

mass number of chlorine-37 – atomic number of chlorine = number of neutrons in chlorine-37

mass number – atomic number = 37 (protons plus neutrons) – 17 protons
= 20 neutrons

An atom of chlorine-37 contains 17 electrons, 17 protons, and 20 neutrons.

4 EVALUATE

The number of protons in a neutral atom equals the number of electrons. And the sum of the protons and neutrons equals the given mass number.

PRACTICE

1. How many protons, electrons, and neutrons are in an atom of bromine-80?

Answer
35 protons, 35 electrons, 45 neutrons

2. Write the nuclear symbol for carbon-13.

Answer
$^{13}_{6}C$

3. Write the hyphen notation for the element that contains 15 electrons and 15 neutrons.

Answer
phosphorus-30

Relative Atomic Masses

Masses of atoms expressed in grams are very small. As we shall see, an atom of oxygen-16, for example, has a mass of 2.657×10^{-23} g. For most chemical calculations it is more convenient to use *relative* atomic masses. As you read in Chapter 2, scientists use standards of measurement that are constant and are the same everywhere. In order to set up a relative scale of atomic mass, one atom has been arbitrarily chosen as the standard and assigned a relative mass value. The masses of all other atoms are expressed in relation to this defined standard.

The standard used by scientists to govern units of atomic mass is the carbon-12 nuclide. It has been arbitrarily assigned a mass of exactly 12 atomic mass units, or 12 amu. *One* **atomic mass unit,** *or 1 amu, is exactly 1/12 the mass of a carbon-12 atom.* The atomic mass of any nuclide is determined by comparing it with the mass of the carbon-12 atom. The hydrogen-1 atom has an atomic mass of *about* 1/12 that of the carbon-12 atom, or about 1 amu. The precise value of the atomic mass of a hydrogen-1 atom is 1.007 825 amu. An oxygen-16 atom has about 16/12 (or 4/3) the mass of a carbon-12 atom. Careful measurements show the atomic mass of oxygen-16 to be 15.994 915 amu. The mass of a magnesium-24 atom is found to be slightly less than twice that of a carbon-12 atom. Its atomic mass is 23.985 042 amu.

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Some additional examples of the atomic masses of the naturally occurring isotopes of several elements are given in Table 3-4 on page 80. Isotopes of an element may occur naturally, or they may be made in the laboratory *(artificial isotopes)*. *Although isotopes have different masses, they do not differ significantly in their chemical behavior.*

The masses of subatomic particles can also be expressed on the atomic mass scale (see Table 3-1). The mass of the electron is 0.000 5486 amu, that of the proton is 1.007 276 amu, and that of the neutron is 1.008 665 amu. Note that the proton and neutron masses are close to but not equal to 1 amu. You have learned that the mass number is the total number of protons and neutrons in the nucleus of an atom. You can now see that the mass number and relative atomic mass of a given nuclide are quite close to each other. They are not identical because the proton and neutron masses deviate slightly from 1 amu and the atomic masses include electrons. Also, as you will read in Chapter 22, a small amount of mass is changed to energy in the creation of a nucleus from protons and neutrons.

Average Atomic Masses of Elements

Most elements occur naturally as mixtures of isotopes, as indicated in Table 3-4. The percentage of each isotope in the naturally occurring element on Earth is nearly always the same, no matter where the element is found. The percentage at which each of an element's isotopes occurs in nature is taken into account when calculating the element's average atomic mass. **Average atomic mass** *is the weighted average of the atomic masses of the naturally occurring isotopes of an element.*

The following is a simple example of how to calculate a *weighted average.* Suppose you have a box containing two sizes of marbles. If 25% of the marbles have masses of 2.00 g each and 75% have masses of 3.00 g each, how is the weighted average calculated? You could count the marbles, calculate the total mass of the mixture, and divide by the total number of marbles. If you had 100 marbles, the calculations would be as follows.

$$25 \text{ marbles} \times 2.00 \text{ g} = 50 \text{ g}$$
$$75 \text{ marbles} \times 3.00 \text{ g} = 225 \text{ g}$$

Adding these masses gives the total mass of the marbles.

$$50 \text{ g} + 225 \text{ g} = 275 \text{ g}$$

Dividing the total mass by 100 gives an average marble mass of 2.75 g.

A simpler method is to multiply the mass of each marble by the decimal fraction representing its percentage in the mixture. Then add the products.

$$25\% = 0.25 \qquad 75\% = 0.75$$
$$(2.00 \text{ g} \times 0.25) + (3.00 \text{ g} \times 0.75) = 2.75 \text{ g}$$

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TABLE 3-4 *Atomic Masses and Abundances of Several Naturally Occurring Isotopes*

Isotope	Mass number	Percentage natural abundance	Atomic mass (amu)	Average atomic mass of element (amu)
Hydrogen-1	1	99.985	1.007 825	1.007 94
Hydrogen-2	2	0.015	2.014 102	
Carbon-12	12	98.90	12 (by definition)	
Carbon-13	13	1.10	13.003 355	12.0111
Carbon-14	14	trace	14.003 242	
Oxygen-16	16	99.762	15.994 915	
Oxygen-17	17	0.038	16.999 131	15.9994
Oxygen-18	18	0.200	17.999 160	
Copper-63	63	69.17	62.929 599	63.546
Copper-65	65	30.83	64.927 793	
Cesium-133	133	100	132.905 429	132.905
Uranium-234	234	0.005	234.040 947	
Uranium-235	235	0.720	235.043 924	238.029
Uranium-238	238	99.275	238.050 784	

Calculating Average Atomic Mass

The average atomic mass of an element depends on both the mass and the relative abundance of each of the element's isotopes. For example, naturally occurring copper consists of 69.17% copper-63, which has an atomic mass of 62.929 599 amu, and 30.83% copper-65, which has an atomic mass of 64.927 793 amu. The average atomic mass of copper can be calculated by multiplying the atomic mass of each isotope by its relative abundance (expressed in decimal form) and adding the results.

$$0.6917 \times 62.929\ 599\ \text{amu} + 0.3083 \times 64.927\ 793\ \text{amu} = 63.55\ \text{amu}$$

The calculated average atomic mass of naturally occurring copper is 63.55 amu.

The average atomic mass is included for the elements listed in Table 3-4. As illustrated in the table, most atomic masses are known to four or more significant figures. *In this book, an element's atomic mass is usually rounded to two decimal places before it is used in a calculation.*

Relating Mass to Numbers of Atoms

The relative atomic mass scale makes it possible to know how many atoms of an element are present in a sample of the element with a measurable mass. Three very important concepts—the mole, Avogadro's number, and molar mass—provide the basis for relating masses in grams to numbers of atoms.

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The Mole

The mole is the SI unit for amount of substance. *A* **mole** *(abbreviated* mol*) is the amount of a substance that contains as many particles as there are atoms in exactly 12 g of carbon-12.* The mole is a counting unit, just like a dozen is. We don't usually order 12 or 24 ears of corn; we order one dozen or two dozen. Similarly, a chemist may want 1 mol of carbon, or 2 mol of iron, or 2.567 mol of calcium. In the sections that follow, you will see how the mole relates to masses of atoms and compounds.

Avogadro's Number

The number of particles in a mole has been experimentally determined in a number of ways. The best modern value is $6.022\ 1367 \times 10^{23}$. This means that exactly 12 g of carbon-12 contains $6.022\ 1367 \times 10^{23}$ carbon-12 atoms. The number of particles in a mole is known as Avogadro's number, named for the nineteenth-century Italian scientist Amedeo Avogadro, whose ideas were crucial in explaining the relationship between mass and numbers of atoms. **Avogadro's number**—*$6.022\ 1367 \times 10^{23}$—is the number of particles in exactly one mole of a pure substance.* For most purposes, Avogadro's number is rounded to 6.022×10^{23}.

To get a sense of how large Avogadro's number is, consider the following: If every person living on Earth (5 billion people) worked to count the atoms in one mole of an element, and if each person counted continuously at a rate of one atom per second, it would take about 4 million years for all the atoms to be counted.

Molar Mass

An alternative definition of *mole* is the amount of a substance that contains Avogadro's number of particles. Can you figure out the approximate mass of one mole of helium atoms? You know that a mole of carbon-12 atoms has a mass of exactly 12 g and that a carbon-12 atom has an atomic mass of 12 amu. The atomic mass of a helium atom is 4.00 amu, which is about one-third the mass of a carbon-12 atom. It follows that a mole of helium atoms will have about one-third the mass of a mole of carbon-12 atoms. Thus, one mole of helium has a mass of about 4.00 g.

The mass of one mole of a pure substance is called the **molar mass** *of that substance.* Molar mass is usually written in units of g/mol. The molar mass of an element is numerically equal to the atomic mass of the element in atomic mass units (which can be found in the periodic table). For example, the molar mass of lithium, Li, is 6.94 g/mol, while the molar mass of mercury, Hg, is 200.59 g/mol (rounding each value to two decimal places).

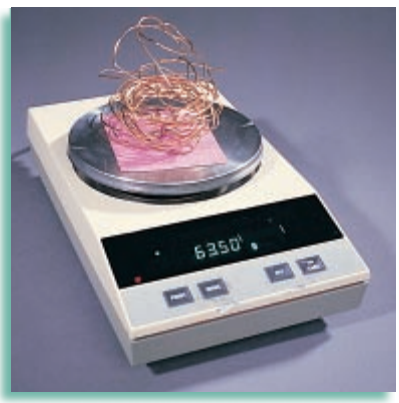
A molar mass of an element contains one mole of atoms. For example, 4.00 g of helium, 6.94 g of lithium, and 200.59 g of mercury all contain a mole of atoms. Figure 3-10 shows molar masses of three common elements.

Gram/Mole Conversions

Chemists use molar mass as a conversion factor in chemical calculations. For example, the molar mass of helium is 4.00 g He/mol He. To

(a)

(b)



(c)

FIGURE 3-10 Shown is approximately one molar mass of each of three elements: (a) carbon (as graphite), (b) iron (nails), and (c) copper (wire).

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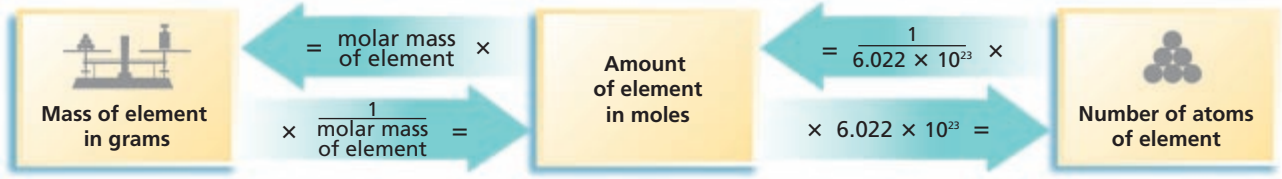
Mass of element in grams
= molar mass of element ×
× 1 / molar mass of element =
Amount of element in moles
= 1 / 6.022 × 10²³ ×
× 6.022 × 10²³ =
Number of atoms of element

FIGURE 3-11 The diagram shows the relationship between mass in grams, amount in moles, and number of atoms of an element in a sample.

find how many grams of helium there are in two moles of helium, multiply by the molar mass.

$$2.00 \text{ mol He} \times \frac{4.00 \text{ g He}}{\text{mol He}} = 8.00 \text{ g He}$$

Figure 3-11 shows how to use molar mass, moles, and Avogadro's number to relate mass in grams, amount in moles, and number of atoms of an element.

SAMPLE PROBLEM 3-2

What is the mass in grams of 3.50 mol of the element copper, Cu?

SOLUTION

1 ANALYZE

Given: 3.50 mol Cu
Unknown: mass of Cu in grams

2 PLAN

amount of Cu in moles ⟶ mass of Cu in grams

According to Figure 3-11, the mass of an element in grams can be calculated by multiplying the amount of the element in moles by the element's molar mass.

$$\text{moles Cu} \times \frac{\text{grams Cu}}{\text{moles Cu}} = \text{grams Cu}$$

3 COMPUTE

The molar mass of copper from the periodic table is rounded to 63.55 g/mol.

$$3.50 \text{ mol Cu} \times \frac{63.55 \text{ g Cu}}{\text{mol Cu}} = 222 \text{ g Cu}$$

4 EVALUATE

Because the amount of copper in moles was given to three significant figures, the answer was rounded to three significant figures. The size of the answer is reasonable because it is somewhat more than 3.5 times 60.

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PRACTICE

1. What is the mass in grams of 2.25 mol of the element iron, Fe?
   Answer
   126 g Fe

2. What is the mass in grams of 0.375 mol of the element potassium, K?
   Answer
   14.7 g K

3. What is the mass in grams of 0.0135 mol of the element sodium, Na?
   Answer
   0.310 g Na

4. What is the mass in grams of 16.3 mol of the element nickel, Ni?
   Answer
   957 g Ni

SAMPLE PROBLEM 3-3

A chemist produced 11.9 g of aluminum, Al. How many moles of aluminum were produced?

SOLUTION

1 ANALYZE

Given: 11.9 g Al
Unknown: amount of Al in moles

2 PLAN

$$\text{mass of Al in grams} \longrightarrow \text{amount of Al in moles}$$

As shown in Figure 3-11, amount in moles can be obtained by *dividing* mass in grams by molar mass, which is mathematically the same as *multiplying* mass in grams by the *reciprocal* of molar mass.

$$\text{grams Al} \times \frac{\text{moles Al}}{\text{grams Al}} = \text{moles Al}$$

3 COMPUTE

The molar mass of aluminum from the periodic table is rounded to 26.98 g/mol.

$$11.9 \text{ g Al} \times \frac{\text{mol Al}}{26.98 \text{ g Al}} = 0.441 \text{ mol Al}$$

4 EVALUATE

The answer is correctly given to three significant figures. The answer is reasonable because 11.9 g is somewhat less than half of 26.98 g.

PRACTICE

1. How many moles of calcium, Ca, are in 5.00 g of calcium?
   Answer
   0.125 mol Ca

2. How many moles of gold, Au, are in 3.60×10^{-10} g of gold?
   Answer
   1.83×10^{-12} mol Au

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Conversions with Avogadro's Number

Figure 3-11 shows that Avogadro's number can be used to find the number of atoms of an element from the amount in moles or to find the amount of an element in moles from the number of atoms. While these types of problems are less common in chemistry than converting between amount in moles and mass in grams, they are useful in demonstrating the meaning of Avogadro's number. Note that in these calculations, Avogadro's number is expressed in units of atoms per mole.

SAMPLE PROBLEM 3-4

How many moles of silver, Ag, are in 3.01×10^{23} atoms of silver?

SOLUTION

1 ANALYZE

Given: 3.01×10^{23} atoms of Ag
Unknown: amount of Ag in moles

2 PLAN

$$\text{number of atoms of Ag} \longrightarrow \text{amount of Ag in moles}$$

From Figure 3-11, we know that number of atoms is converted to amount in moles by dividing by Avogadro's number. This is equivalent to multiplying numbers of atoms by the reciprocal of Avogrado's number.

$$\text{Ag atoms} \times \frac{\text{moles Ag}}{\text{Avogadro's number of Ag atoms}} = \text{moles Ag}$$

3 COMPUTE

$$3.01 \times 10^{23}\ \cancel{\text{Ag atoms}} \times \frac{\text{mol Ag}}{6.022 \times 10^{23}\ \cancel{\text{Ag atoms}}} = 0.500\ \text{mol Ag}$$

4 EVALUATE

The answer is correct—units cancel correctly and the number of atoms is exactly one-half of Avogadro's number.

PRACTICE

1. How many moles of lead, Pb, are in 1.50×10^{12} atoms of lead?
   Answer
   2.49×10^{-12} mol Pb
2. How many moles of tin, Sn, are in 2500 atoms of tin?
   Answer
   4.2×10^{-21} mol Sn
3. How many atoms of aluminum, Al, are in 2.75 mol of aluminum?
   Answer
   1.66×10^{24} atoms Al

SAMPLE PROBLEM 3-5

What is the mass in grams of 1.20×10^{8} atoms of copper, Cu?

SOLUTION

1 ANALYZE

Given: 1.20×10^{8} atoms of Cu
Unknown: mass of Cu in grams

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2 PLAN

number of atoms of Cu ⟶ amount of Cu in moles ⟶ mass of Cu in grams

As indicated in Figure 3-11, the given number of atoms must first be converted to amount in moles by dividing by Avogadro's number. Amount in moles is then multiplied by molar mass to yield mass in grams.

$$\text{Cu atoms} \times \frac{\text{moles Cu}}{\text{Avogadro's number of Cu atoms}} \times \frac{\text{grams Cu}}{\text{moles Cu}} = \text{grams Cu}$$

3 COMPUTE

The molar mass of copper from the periodic table is rounded to 63.55 g/mol.

$$1.20 \times 10^{8}\ \cancel{\text{Cu atoms}} \times \frac{1\ \cancel{\text{mol Cu}}}{6.022 \times 10^{23}\ \cancel{\text{Cu atoms}}} \times \frac{63.55\ \text{g Cu}}{\cancel{\text{mol Cu}}} = 1.27 \times 10^{-14}\ \text{g Cu}$$

4 EVALUATE

Units cancel correctly to give the answer in grams. The size of the answer is reasonable—10^{8} has been divided by about 10^{24} and multiplied by about 10^{2}.

PRACTICE

1. What is the mass in grams of 7.5×10^{15} atoms of nickel, Ni?

   Answer
   7.3×10^{-7} g Ni

2. How many atoms of sulfur, S, are in 4.00 g of sulfur?

   Answer
   7.51×10^{22} atoms S

3. What mass of gold, Au, contains the same number of atoms as 9.0 g of aluminum, Al?

   Answer
   66 g Au

SECTION REVIEW

1. Define each of the following:
   a. atomic number
   b. mass number
   c. relative atomic mass
   d. average atomic mass
   e. mole
   f. Avogadro's number
   g. molar mass
   h. isotope
2. Determine the number of protons, electrons, and neutrons in each of the following isotopes:
   a. sodium-23
   b. calcium-40
   c. $^{64}_{29}\text{Cu}$
   d. $^{108}_{47}\text{Ag}$
3. Write the nuclear symbol and hyphen notation for each of the following isotopes:
   a. mass number of 28 and atomic number of 14
   b. 26 protons and 30 neutrons
   c. 56 electrons and 82 neutrons
4. To two decimal places, what is the relative atomic mass and the molar mass of the element potassium, K?
5. Determine the mass in grams of the following:
   a. 2.00 mol N
   b. 3.01×10^{23} atoms Cl
6. Determine the amount in moles of the following:
   a. 12.15 g Mg
   b. 1.50×10^{23} atoms F
7. Determine the number of atoms in the following:
   a. 2.50 mol Zn
   b. 1.50 g C

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CHAPTER 3 REVIEW

CHAPTER SUMMARY

3-1

- The *idea* of atoms has been around since the time of the ancient Greeks. In the nineteenth century, John Dalton proposed a *scientific theory* of atoms that can still be used to explain properties of many chemicals today.
- When elements react to form compounds, they combine in fixed proportions by mass.
- Matter and its mass cannot be created or destroyed in chemical reactions.
- The mass ratio of the elements that make up a given compound is always the same, regardless of how much of the compound there is or how it was formed.
- If two or more different compounds are composed of the same two elements, then the ratio of the masses of the second element combined with a certain mass of the first element can be expressed as a ratio of small whole numbers.

Vocabulary

law of conservation of mass (66) law of definite proportions (66) law of multiple proportions (66)

3-2

- Cathode-ray tubes supplied evidence of the existence of electrons, which are negatively charged subatomic particles that have relatively little mass.
- Rutherford found evidence for the existence of the atomic nucleus—a positively charged, very dense core within the atom—by bombarding metal foil with a beam of positively charged particles.
- Atomic nuclei are composed of protons, which have an electric charge of +1, and (in all but one case) neutrons, which have no electric charge.
- Isotopes of an element differ in the number of neutrons in their nuclei.
- Atomic nuclei have radii of about 0.001 pm (pm = picometers; 1 pm = 10^{-12} m), while atoms have radii of about 40–270 pm.

Vocabulary

atom (70) nuclear forces (74)

3-3

- The atomic number of an element is equal to the number of protons in the nucleus of an atom of that element.
- The mass number is equal to the total number of protons and neutrons in the nucleus of an atom of that element.
- The relative atomic mass unit (amu) is based on the carbon-12 atom and is a convenient unit for measuring the mass of atoms. It equals $1.660\ 540 \times 10^{-24}$ g.
- The average atomic mass of an element is found by calculating the weighted average of the atomic masses of the naturally occurring isotopes of the element.
- Avogadro's number is equal to approximately $6.022\ 137 \times 10^{23}$. It is equal to the number of atoms in exactly 12 g of carbon-12. A sample that contains a number of particles equal to Avogadro's number contains a mole of those particles.
- The molar mass of an element is the mass of one mole of atoms of that element.

Vocabulary

atomic mass unit (78) Avogadro's number (81) mass number (76) mole (81)
atomic number (75) isotopes (76) molar mass (81) nuclide (77)
average atomic mass (79)

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REVIEWING CONCEPTS

1. Explain each of the following in terms of Dalton's atomic theory:
a. the law of conservation of mass
b. the law of definite proportions
c. the law of multiple proportions (3-1)

2. According to the law of conservation of mass, if element A has an atomic mass of 2 mass units and element B has an atomic mass of 3 mass units, what mass would be expected for compound AB? for compound A_2B_3? (3-1)

3. a. What is an atom?
b. What two regions make up all atoms? (3-2)

4. Describe at least four properties of electrons that were determined based on the experiments of Thomson and Millikan. (3-2)

5. Summarize Rutherford's model of an atom, and explain how he developed this model based on the results of his famous gold-foil experiment. (3-2)

6. What one number identifies an element? (3-2)

7. a. What are isotopes?
b. How are the isotopes of a particular element alike?
c. How are they different? (3-3)

8. Copy and complete the following table concerning the three isotopes of silicon, Si. (Hint: See Sample Problem 3-1.) (3-3)

Isotope	Number of protons	Number of electrons	Number of neutrons
Si-28			
Si-29			
Si-30			

9. a. What is the atomic number of an element?
b. What is the mass number of an isotope?
c. In the nuclear symbol for deuterium, $^{2}_{1}H$, identify the atomic number and the mass number. (3-3)

10. What is a nuclide? (3-3)

11. Use the periodic table and the information that follows to write the hyphen notation for each isotope described.
a. atomic number = 2, mass number = 4
b. atomic number = 8, mass number = 16
c. atomic number = 19, mass number = 39 (3-3)

12. a. What nuclide is used as the standard in the relative scale for atomic masses?
b. What is its assigned atomic mass? (3-3)

13. What is the atomic mass of an atom if its mass is approximately equal to the following?
a. $\frac{1}{3}$ that of carbon-12
b. 4.5 times as much as carbon-12 (3-3)

14. a. What is the definition of a mole?
b. What is the abbreviation for mole?
c. How many particles are in one mole?
d. What name is given to the number of particles in a mole? (3-3)

15. a. What is the molar mass of an element?
b. To two decimal places, write the molar masses of carbon, neon, iron, and uranium. (3-3)

16. Suppose you have a sample of an element.
a. How is the mass in grams of the element converted to amount in moles?
b. How is the mass in grams of the element converted to number of atoms? (3-3)

PROBLEMS

The Mole and Molar Mass

17. What is the mass in grams of each of the following? (Hint: See Sample Problems 3-2 and 3-5.)
a. 1.00 mol Li
b. 1.00 mol Al
c. 1.00 molar mass Ca
d. 1.00 molar mass Fe
e. 6.022×10^{23} atoms C
f. 6.022×10^{23} atoms Ag

18. How many moles of atoms are there in each of the following? (Hint: See Sample Problems 3-3 and 3-4.)
a. 6.022×10^{23} atoms Ne
b. 3.011×10^{23} atoms Mg
c. 3.25×10^{5} g Pb
d. 4.50×10^{-12} g O

Relative Atomic Mass

19. Three isotopes of argon occur in nature—$^{36}_{18}Ar$, $^{38}_{18}Ar$, and $^{40}_{18}Ar$. Calculate the average atomic mass of argon to two decimal places, given the following relative atomic masses and abundances of each of the isotopes: argon-36 (35.97 amu; 0.337%), argon-38 (37.96 amu; 0.063%), and argon-40 (39.96 amu; 99.600%).

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20. Naturally occurring boron is 80.20% boron-11 (atomic mass = 11.01 amu) and 19.80% of some other isotopic form of boron. What must the atomic mass of this second isotope be in order to account for the 10.81 amu average atomic mass of boron? (Write the answer to two decimal places.)

Number of Atoms in a Sample

21. How many atoms are there in each of the following?
a. 1.50 mol Na
b. 6.755 mol Pb
c. 7.02 g Si

22. What is the mass in grams of each of the following?
a. 3.011×10^{23} atoms F
b. 1.50×10^{23} atoms Mg
c. 4.50×10^{12} atoms Cl
d. 8.42×10^{18} atoms Br
e. 25 atoms W
f. 1 atom Au

23. Determine the number of atoms in each of the following:
a. 5.40 g B
b. 0.250 mol S
c. 0.0384 mol K
d. 0.025 50 g Pt
e. 1.00×10^{-10} g Au

MIXED REVIEW

24. Determine the mass in grams of each of the following:
a. 3.00 mol Al
b. 2.56×10^{24} atoms Li
c. 1.38 mol N
d. 4.86×10^{24} atoms Au
e. 6.50 mol Cu
f. 2.57×10^{8} mol S
g. 1.05×10^{18} atoms Hg

25. Copy and complete the following table concerning the properties of subatomic particles:

Particle	Symbol	Mass number	Actual mass	Relative charge
Electron				
Proton				
Neutron				

26. a. How is an atomic mass unit (amu) related to the mass of a carbon-12 atom?
b. What is the relative atomic mass of an atom?

27. a. What is the nucleus of an atom?
b. Who is credited with the discovery of the atomic nucleus?
c. Identify the two kinds of particles contained in the nucleus.

28. How many moles of atoms are there in each of the following?
a. 40.1 g Ca
b. 11.5 g Na
c. 5.87 g Ni
d. 150 g S
e. 2.65 g Fe
f. 0.007 50 g Ag
g. 2.25×10^{25} atoms Zn
h. 50.0 atoms Ba

29. State the law of multiple proportions, and give an example of two compounds that illustrate the law.

30. What is the approximate atomic mass of an atom if its mass is
a. 12 times that of carbon-12?
b. $\frac{1}{2}$ that of carbon-12?

31. What is an electron?

CRITICAL THINKING

32. Organizing Ideas Using two chemical compounds as an example, describe the difference between the law of definite proportions and the law of multiple proportions.

33. Constructing Models As described on pages 70 to 74, the structure of the atom was determined from observations made in painstaking experimental research. Suppose a series of experiments revealed that when an electric current is passed through gas at low pressure, the surface of the cathode-ray tube opposite the anode glows. In addition, a paddle wheel placed in the tube rolls from the anode toward the cathode when the current is on.
a. In which direction do particles pass through the gas?
b. What charge do the particles possess?

34. Inferring Relationships How much mass is converted into energy during the creation of the nucleus of a $^{235}_{92}U$ nuclide from 92 protons, 143 neutrons, and 92 electrons? (Hint: See Section 22-1.)

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TECHNOLOGY & LEARNING

35. Graphing Calculator Calculate Numbers of Protons, Electrons, and Neutrons. A graphing calculator can run a program that calculates the numbers of protons, electrons, and neutrons given the atomic mass and numbers for an atom. For example, given a calcium-40 atom, you will calculate the number of protons, electrons, and neutrons in the atom.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data sets and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data sets, answer these questions.

a. Which element has the most protons?
b. How many neutrons does mercury-201 have?
c. Carbon-12 and carbon-14 have the same atomic number. Do they have the same number of neutrons? Why or why not?

HANDBOOK SEARCH

36. Group 14 of the *Elements Handbook* describes the reactions that produce CO and CO_2. Review this section to answer the following:

a. When a fuel burns, what determines whether CO or CO_2 will be produced?
b. What happens in the body if hemoglobin picks up CO instead of CO_2 or O_2?
c. Why is CO poisoning most likely to occur in homes that are well sealed during cold winter months?

RESEARCH & WRITING

37. Prepare a report on the series of experiments conducted by Sir James Chadwick that led to the discovery of the neutron.

38. Write a report on the contributions of Amedeo Avogadro that led to the determination of the value of Avogadro's number.

39. Trace the development of the electron microscope, and cite some of its many uses.

40. The study of atomic structure and the nucleus produced a new field of medicine called nuclear medicine. Describe the use of radioactive tracers to detect and treat diseases.

ALTERNATIVE ASSESSMENT

41. Observe a cathode-ray tube in operation, and write a description of your observations.

42. Performance Assessment Using colored clay, build a model of the nucleus of each of carbon's three naturally occurring isotopes: carbon-12, carbon-13, and carbon-14. Specify the number of electrons that would surround each nucleus.

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CHAPTER 4

Arrangement of Electrons in Atoms

The emission of light is fundamentally related to the behavior of electrons.

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The Development of a New Atomic Model

SECTION 4-1

Objectives

- Explain the mathematical relationship among the speed, wavelength, and frequency of electromagnetic radiation.
- Discuss the dual wave-particle nature of light.
- Discuss the significance of the photoelectric effect and the line-emission spectrum of hydrogen to the development of the atomic model.
- Describe the Bohr model of the hydrogen atom.

The Rutherford model of the atom was an improvement over previous models, but it was incomplete. It did not explain where the atom's negatively charged electrons are located in the space surrounding its positively charged nucleus. After all, it was well known that oppositely charged particles attract each other. So what prevented the negative electrons from being drawn into the positive nucleus?

In the early twentieth century, a new atomic model evolved as a result of investigations into the absorption and emission of light by matter. The studies revealed an intimate relationship between light and an atom's electrons. This new understanding led directly to a revolutionary view of the nature of energy, matter, and atomic structure.

Properties of Light

Before 1900, scientists thought light behaved solely as a wave. This belief changed when it was later discovered that light also has particle-like characteristics. Still, many of light's properties can be described in terms of waves. A quick review of these wavelike properties will help you understand the basic theory of light as it existed at the beginning of the twentieth century.

The Wave Description of Light

Visible light is a kind of **electromagnetic radiation,** *which is a form of energy that exhibits wavelike behavior as it travels through space.* Other kinds of electromagnetic radiation include X rays, ultraviolet and infrared light, microwaves, and radio waves. *Together, all the forms of electromagnetic radiation form the* **electromagnetic spectrum.** The electromagnetic spectrum is represented in Figure 4-1 on page 92. All forms of electromagnetic radiation move at a constant speed of about 3.0×10^8 meters per second (m/s) through a vacuum and at slightly slower speeds through matter. Because air is mostly space, the value of 3.0×10^8 m/s is also light's approximate speed through air.

The significant feature of wave motion is its repetitive nature, which can be characterized by the measurable properties of wavelength and frequency. **Wavelength** (λ) *is the distance between corresponding points on adjacent waves.* Depending on the particular form of electromagnetic radiation, the unit for wavelength is the meter, centimeter, or nanome-

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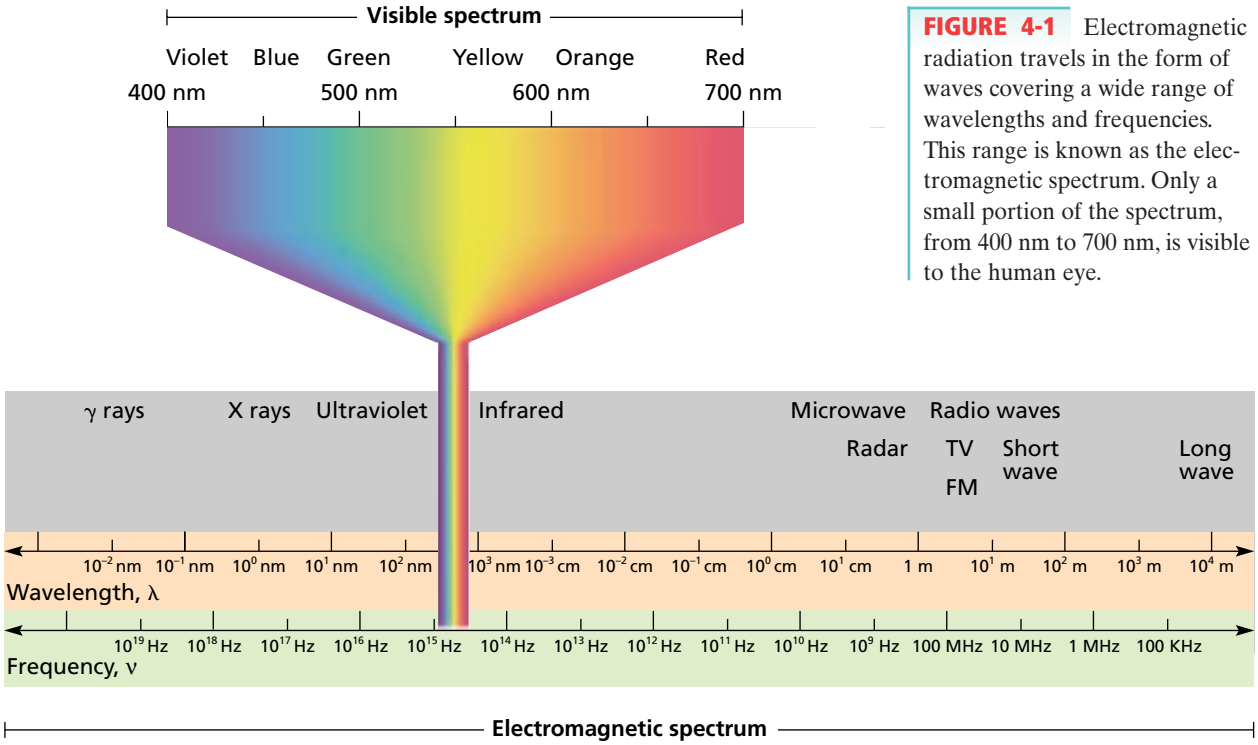

FIGURE 4-1 Electromagnetic radiation travels in the form of waves covering a wide range of wavelengths and frequencies. This range is known as the electromagnetic spectrum. Only a small portion of the spectrum, from 400 nm to 700 nm, is visible to the human eye.

ter ($1 \text{ nm} = 1 \times 10^{-9}$ m), as shown in Figure 4-1. **Frequency** (ν) *is defined as the number of waves that pass a given point in a specific time, usually one second.* Frequency is expressed in waves/second. One wave/second is called a hertz (Hz), named for Heinrich Hertz, who was a pioneer in the study of electromagnetic radiation. Figure 4-2 illustrates the properties of wavelength and frequency for a familiar kind of wave, a wave on the surface of water. The wavelength in Figure 4-2(a) has a longer wavelength and a lower frequency than the wave in Figure 4-2(b).

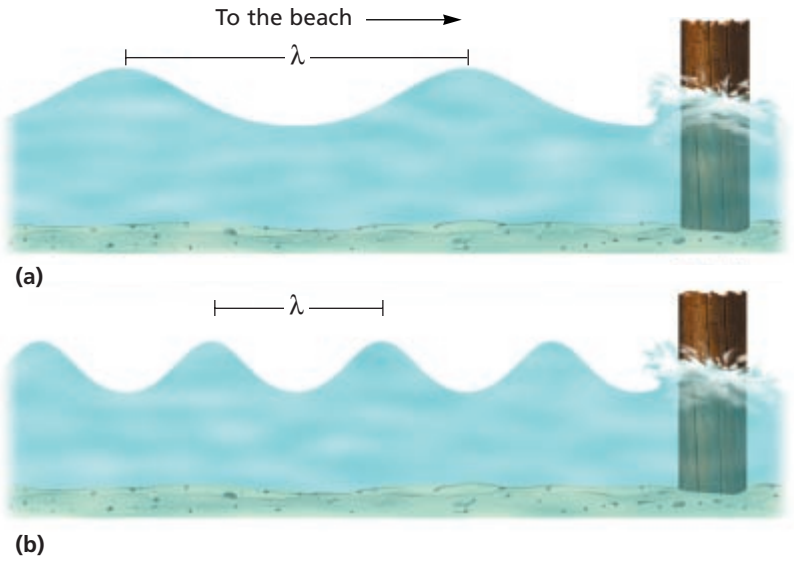

FIGURE 4-2 The distance between any two corresponding points on one of these water waves, such as from crest to crest, is the wave's wavelength, λ. We can measure the wave's frequency, ν, by observing how often the water level rises and falls at a given point, such as at the post.

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Frequency and wavelength are mathematically related to each other. For electromagnetic radiation, this relationship is written as follows.

$$c = \lambda\nu$$

In the equation, c is the speed of light, λ is the wavelength of the electromagnetic wave, and ν is the frequency of the electromagnetic wave. Because c is the same for all electromagnetic radiation, the product $\lambda\nu$ is a constant. Consequently, we know that λ is inversely proportional to ν. In other words, as the wavelength of light decreases, its frequency increases, and vice versa.

The Photoelectric Effect

In the early 1900s, scientists conducted two experiments involving interactions of light and matter that could not be explained by the wave theory of light. One experiment involved a phenomenon known as the photoelectric effect. *The* **photoelectric effect** *refers to the emission of electrons from a metal when light shines on the metal,* as illustrated in Figure 4-3.

The mystery of the photoelectric effect involved the frequency of the light striking the metal. For a given metal, no electrons were emitted if the light's frequency was below a certain minimum—regardless of how long the light was shone. Light was known to be a form of energy, capable of knocking loose an electron from a metal. But the wave theory of light predicted that light of any frequency could supply enough energy to eject an electron. Scientists couldn't explain why the light had to be of a minimum frequency in order for the photoelectric effect to occur.

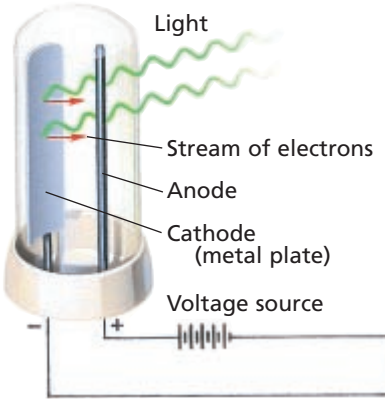

FIGURE 4-3 The photoelectric effect: electromagnetic radiation strikes the surface of the metal, ejecting electrons from the metal and creating an electric current.

The Particle Description of Light

The explanation of the photoelectric effect dates back to 1900, when German physicist Max Planck was studying the emission of light by hot objects. He proposed that a hot object does not emit electromagnetic energy continuously, as would be expected if the energy emitted were in the form of waves. Instead, Planck suggested that the object emits energy in small, specific amounts called quanta. *A* **quantum** *is the minimum quantity of energy that can be lost or gained by an atom.* Planck proposed the following relationship between a quantum of energy and the frequency of radiation.

$$E = h\nu$$

In the equation, E is the energy, in joules, of a quantum of radiation, ν is the frequency of the radiation emitted, and h is a fundamental physical constant now known as Planck's constant; $h = 6.626 \times 10^{-34}$ J·s.

In 1905, Albert Einstein expanded on Planck's theory by introducing the radical idea that electromagnetic radiation has a dual wave-particle nature. While light exhibits many wavelike properties, it can also be

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thought of as a stream of particles. Each particle of light carries a quantum of energy. Einstein called these particles photons. *A* **photon** *is a particle of electromagnetic radiation having zero mass and carrying a quantum of energy.* The energy of a particular photon depends on the frequency of the radiation.

$$E_{photon} = h\nu$$

Einstein explained the photoelectric effect by proposing that electromagnetic radiation is absorbed by matter only in whole numbers of photons. In order for an electron to be ejected from a metal surface, the electron must be struck by a single photon possessing at least the minimum energy required to knock the electron loose. According to the equation $E_{photon} = h\nu$, this minimum energy corresponds to a minimum frequency. If a photon's frequency is below the minimum, then the electron remains bound to the metal surface. Electrons in different metals are bound more or less tightly, so different metals require different minimum frequencies to exhibit the photoelectric effect.

The Hydrogen-Atom Line-Emission Spectrum

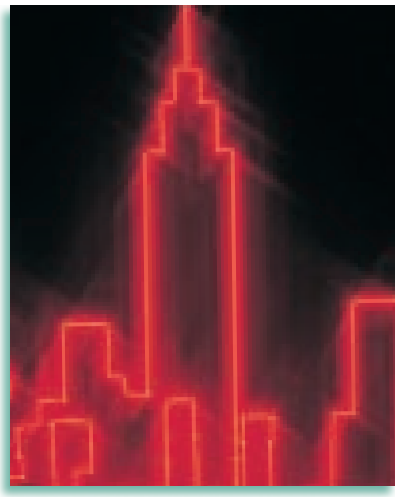

FIGURE 4-4 Excited neon atoms emit light when falling back to the ground state or to a lower-energy excited state.

When current is passed through a gas at low pressure, the potential energy of some of the gas atoms increases. *The lowest energy state of an atom is its* **ground state.** *A state in which an atom has a higher potential energy than it has in its ground state is an* **excited state.** When an excited atom returns to its ground state, it gives off the energy it gained in the form of electromagnetic radiation. The production of colored light in neon signs, as shown in Figure 4-4, is a familiar example of this process.

When investigators passed electric current through a vacuum tube containing hydrogen gas at low pressure, they observed the emission of a characteristic pinkish glow. *When a narrow beam of the emitted light was shined through a prism, it was separated into a series of specific frequencies (and therefore specific wavelengths, $\lambda = c/\nu$) of visible light.* The bands of light were part of what is known as hydrogen's **line-emission spectrum.** The production of hydrogen's line-emission spectrum is illustrated in Figure 4-5. Additional series of lines were discovered in the ultraviolet and infrared regions of hydrogen's line-emission spectrum. The wavelengths of some of the spectral series are shown in Figure 4-6. They are known as the Lyman, Balmer, and Paschen series, after their discoverers.

Classical theory predicted that the hydrogen atoms would be excited by whatever amount of energy was added to them. Scientists had thus expected to observe *the emission of a continuous range of frequencies of electromagnetic radiation,* that is, a **continuous spectrum.** Why had the hydrogen atoms given off only specific frequencies of light? Attempts to explain this observation led to an entirely new theory of the atom called *quantum theory.*

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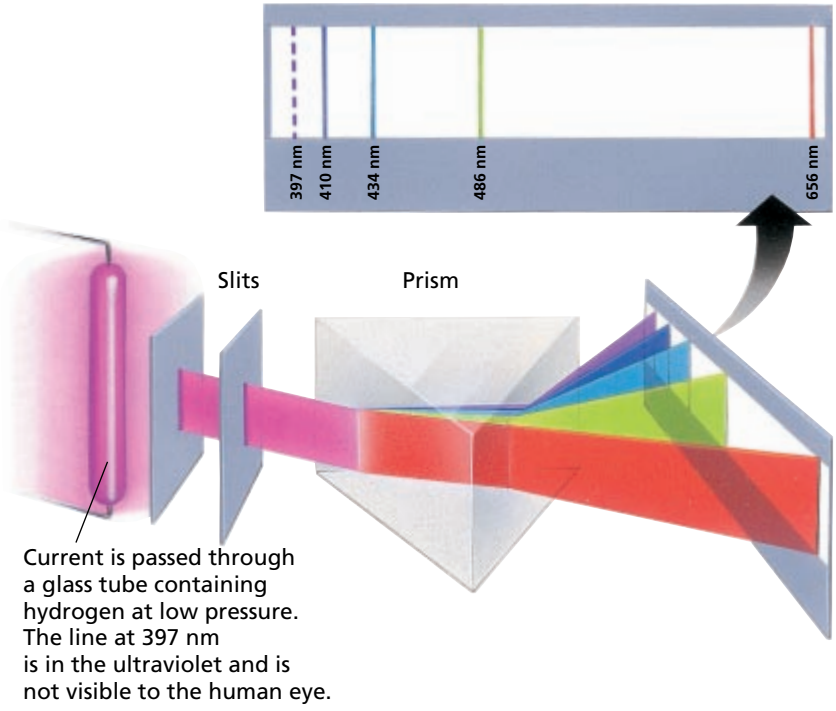
397 nm
410 nm
434 nm
486 nm
656 nm
Slits
Prism
Current is passed through a glass tube containing hydrogen at low pressure. The line at 397 nm is in the ultraviolet and is not visible to the human eye.

FIGURE 4-5 Excited hydrogen atoms emit a pinkish glow. When the visible portion of the emitted light is passed through a prism, it is separated into specific wavelengths that are part of hydrogen's line-emission spectrum. The line at 397 nm is in the ultraviolet and is not visible to the human eye.

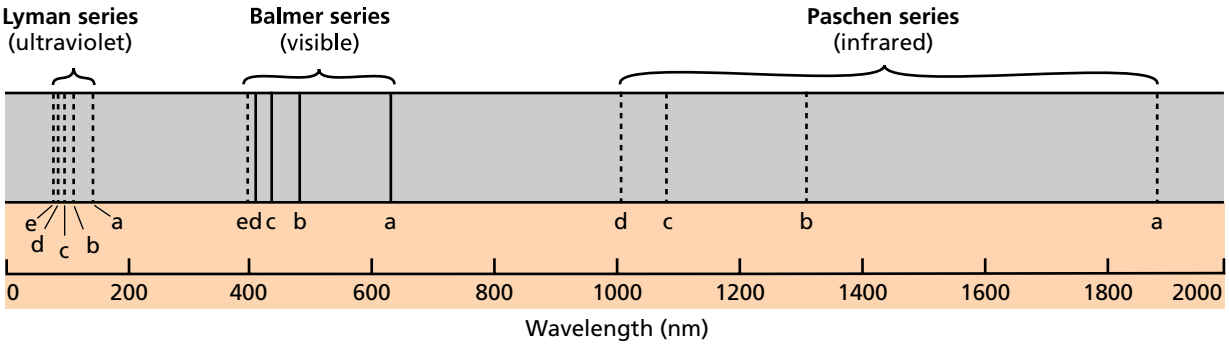

FIGURE 4-6 A series of specific wavelengths of emitted light makes up hydrogen's line-emission spectrum. The letters below the lines label hydrogen's various energy-level transitions. Niels Bohr's model of the hydrogen atom provided an explanation for these transitions.

Whenever an excited hydrogen atom falls back from an excited state to its ground state or to a lower-energy excited state, it emits a photon of radiation. The energy of this photon ($E_{photon} = h\nu$) is equal to the difference in energy between the atom's initial state and its final state, as illustrated in Figure 4-7. The fact that hydrogen atoms emit only specific frequencies of light indicated that the energy differences between the atoms' energy states were fixed. This suggested that the electron of a hydrogen atom exists only in very specific energy states.

In the late nineteenth century, a mathematical relationship that related the various wavelengths of hydrogen's line-emission spectrum was discovered. The challenge facing scientists was to provide a model of the hydrogen atom that accounted for this relationship.

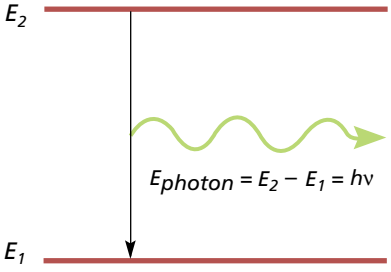

FIGURE 4-7 When an excited atom with energy E_2 falls back to energy E_1, it releases a photon that has energy $E_2 - E_1 = E_{photon} = h\nu$.

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Bohr Model of the Hydrogen Atom

The puzzle of the hydrogen-atom spectrum was solved in 1913 by the Danish physicist Niels Bohr. He proposed a model of the hydrogen atom that linked the atom's electron with photon emission. According to the model, the electron can circle the nucleus only in allowed paths, or *orbits*. When the electron is in one of these orbits, the atom has a definite, fixed energy. The electron, and therefore the hydrogen atom, is in its lowest energy state when it is in the orbit closest to the nucleus. This orbit is separated from the nucleus by a large empty space where the electron cannot exist. The energy of the electron is higher when it is in orbits that are successively farther from the nucleus.

The electron orbits or atomic energy levels in Bohr's model can be compared to the rungs of a ladder. When you are standing on a ladder, your feet are on one rung or another. The amount of potential energy that you possess corresponds to standing on the first rung, the second rung, and so forth. Your energy cannot correspond to standing between two rungs because you cannot stand in midair. In the same way, an electron can be in one orbit or another, but not in between.

How does Bohr's model of the hydrogen atom explain the observed spectral lines? While in an orbit, the electron can neither gain nor lose energy. It can, however, move to a higher energy orbit by gaining an amount of energy equal to the difference in energy between the higher-energy orbit and the initial lower-energy orbit. When a hydrogen atom is in an excited state, its electron is in a higher-energy orbit. When the atom falls back from the excited state, the electron drops down to a lower-energy orbit. In the process, a photon is emitted that has an energy equal to the energy difference between the initial higher-energy orbit and the final lower-energy orbit. Absorption and emission of radiation according to the Bohr model of the hydrogen atom are illustrated in Figure 4-8. The energy of each emitted photon corresponds to a particular frequency of emitted radiation, $E_{photon} = h\nu$.

Based on the wavelengths of hydrogen's line-emission spectrum, Bohr calculated the energies that an electron would have in the allowed energy levels for the hydrogen atom. He then used these values to show

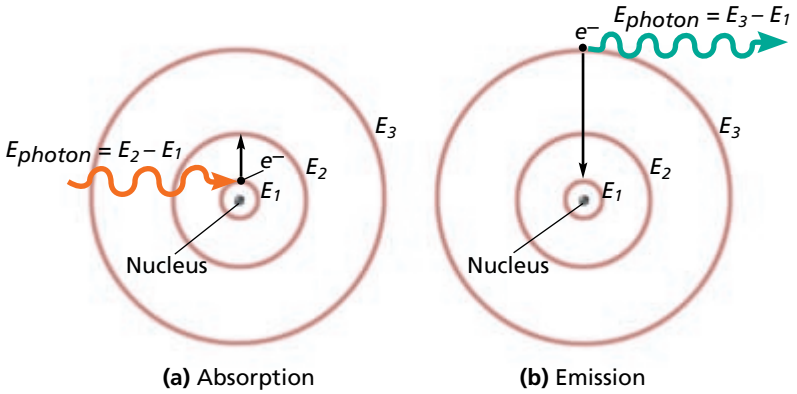

FIGURE 4-8 (a) Absorption and (b) emission of a photon by a hydrogen atom according to Bohr's model. The frequencies of light that can be absorbed and emitted are restricted because the electron can only be in orbits corresponding to the energies E_1, E_2, E_3, and so forth.

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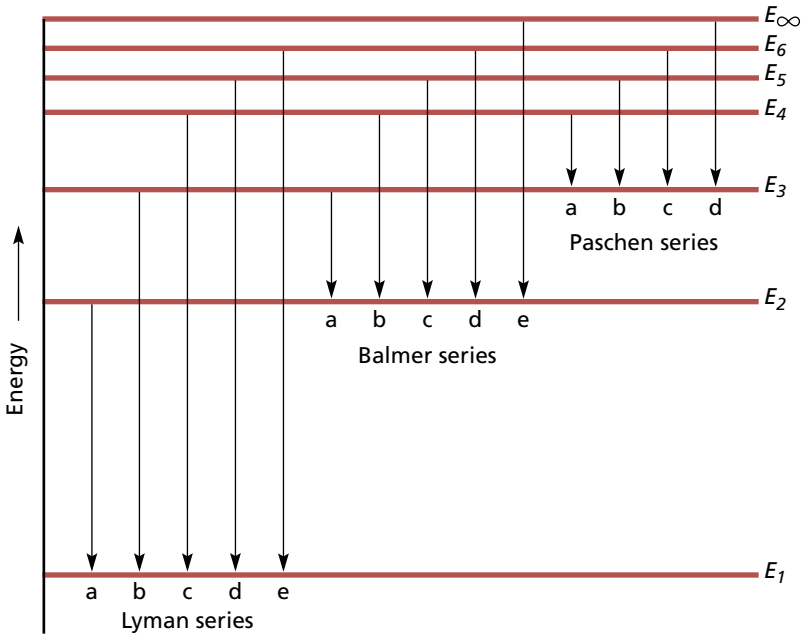

FIGURE 4-9 This electron energy-level diagram for hydrogen shows the energy transitions for the Lyman, Balmer, and Paschen spectral series. Bohr's model of the atom accounted mathematically for the energy of each of the transitions shown.

mathematically how the various spectral series of hydrogen were produced. The Lyman spectral series, for example, was shown to be the result of electrons dropping from various higher-energy levels to the ground-state energy level.

Bohr's calculated values agreed with the experimentally observed values for the lines in each series. The origins of several of the series of lines in hydrogen's line-emission spectrum are shown in Figure 4-9.

The success of Bohr's model of the hydrogen atom in explaining observed spectral lines led many scientists to conclude that a similar model could be applied to all atoms. It was soon recognized, however, that Bohr's approach did not explain the spectra of atoms with more than one electron. Nor did Bohr's theory explain the chemical behavior of atoms.

SECTION REVIEW

1. What was the major shortcoming of Rutherford's model of the atom?
2. Write and label the equation that relates the speed, wavelength, and frequency of electromagnetic radiation.
3. Define the following:
   a. electromagnetic radiation
   b. wavelength
   c. frequency
   d. quantum
   e. photon
4. What is meant by the dual wave-particle nature of light?
5. Describe the Bohr model of the hydrogen atom.

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SECTION 4-2

The Quantum Model of the Atom

Objectives

- Discuss Louis de Broglie's role in the development of the quantum model of the atom.
- Compare and contrast the Bohr model and the quantum model of the atom.
- Explain how the Heisenberg uncertainty principle and the Schrödinger wave equation led to the idea of atomic orbitals.
- List the four quantum numbers, and describe their significance.
- Relate the number of sublevels corresponding to each of an atom's main energy levels, the number of orbitals per sublevel, and the number of orbitals per main energy level.

To the scientists of the early twentieth century, Bohr's model of the hydrogen atom contradicted common sense. Why did hydrogen's electron exist around the nucleus only in certain allowed orbits with definite energies? Why couldn't the electron exist in a limitless number of orbits with slightly different energies? To explain why atomic energy states are quantized, scientists had to change the way they viewed the nature of the electron.

Electrons as Waves

The investigations into the photoelectric effect and hydrogen atomic emission revealed that light could behave as both a wave and a particle. Could electrons have a dual wave-particle nature as well? In 1924, the French scientist Louis de Broglie asked himself this very question. And the answer that he proposed led to a revolution in our basic understanding of matter.

De Broglie pointed out that in many ways the behavior of Bohr's quantized electron orbits was similar to the known behavior of waves. For example, scientists at the time knew that any wave confined to a space can have only certain frequencies. De Broglie suggested that electrons be considered waves confined to the space around an atomic nucleus. It followed that the electron waves could exist only at specific frequencies. And according to the relationship $E = h\nu$, these frequencies corresponded to specific energies—the quantized energies of Bohr's orbits.

Other aspects of de Broglie's hypothesis that electrons have wave-like properties were soon confirmed by experiments. Investigators demonstrated that electrons, like light waves, can be bent, or diffracted. *Diffraction* refers to the bending of a wave as it passes by the edge of an object, such as the edge of an atom in a crystal. Diffraction experiments and other investigations also showed that electron beams, like waves, can interfere with each other. *Interference* occurs when waves overlap (see the Quick Lab on page 100). This overlapping results in a reduction of energy in some areas and an increase of energy in others. The effects of diffraction and interference can be seen in Figure 4-10.

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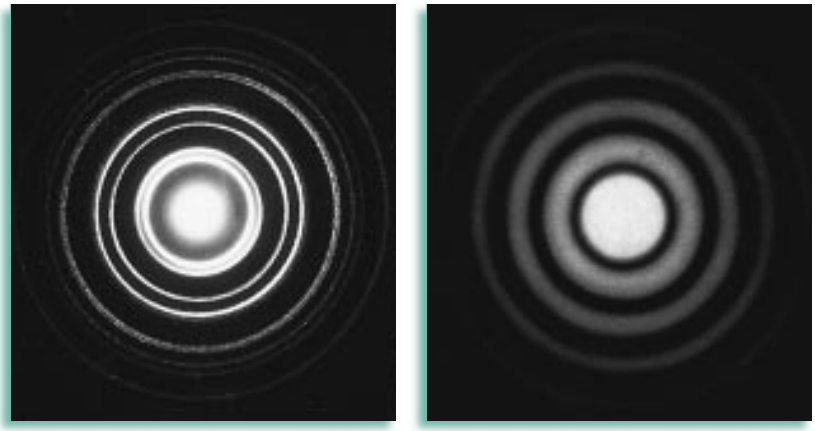

(a) (b)

FIGURE 4-10 Diffraction patterns produced by (a) a beam of electrons passed through a crystal and (b) a beam of visible light passed through a tiny aperture. Each pattern shows the results of bent waves that have interfered with each other. The bright areas correspond to areas of increased energy, while the dark areas correspond to areas of decreased energy.

The Heisenberg Uncertainty Principle

The idea of electrons having a dual wave-particle nature troubled scientists. If electrons are both particles and waves, then where are they in the atom? To answer this question, it is important to consider a proposal first made in 1927 by the German theoretical physicist Werner Heisenberg.

Heisenberg's idea involved the detection of electrons. Electrons are detected by their interaction with photons. Because photons have about the same energy as electrons, any attempt to locate a specific electron with a photon knocks the electron off its course. As a result, there is always a basic uncertainty in trying to locate an electron (or any other particle). *The* **Heisenberg uncertainty principle** *states that it is impossible to determine simultaneously both the position and velocity of an electron or any other particle*. Although it was difficult for scientists to accept this fact at the time, it has proven to be one of the fundamental principles of our present understanding of light and matter.

The Schrödinger Wave Equation

In 1926, the Austrian physicist Erwin Schrödinger used the hypothesis that electrons have a dual wave-particle nature to develop an equation that treated electrons in atoms as waves. Unlike Bohr's theory, which assumed quantization as a fact, quantization of electron energies was a natural outcome of Schrödinger's equation. Only waves of specific energies, and therefore frequencies, provided solutions to the equation. Together with the Heisenberg uncertainty principle, the Schrödinger wave equation laid the foundation for modern quantum theory. **Quantum theory** *describes mathematically the wave properties of electrons and other very small particles.*

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Quick LAB

The Wave Nature of Light: Interference

Wear Safety Goggles and an Apron.

Materials

- scissors
- manila folders
- thumbtack
- masking tape
- aluminum foil
- white poster board or cardboard
- flashlight

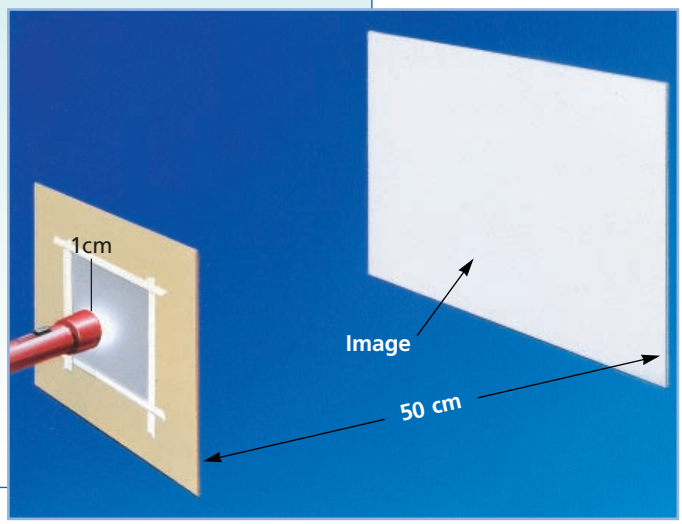
Question

Does light show the wave property of interference when a beam of light is projected through a pinhole onto a screen?

Procedure

Record all your observations.

1. To make the pinhole screen, cut a 20 cm × 20 cm square from a manila folder. In the center of the square, cut a 2 cm square hole. Cut a 7 cm × 7 cm square of aluminum foil. Using a thumbtack, make a pinhole in the center of the foil square. Tape the aluminum foil over the 2 cm square hole, making sure the pinhole is centered as shown in the diagram.
2. Use white poster board to make a projection screen 35 cm × 35 cm.
3. In a dark room, center the light beam from a flashlight on the pinhole. Hold the flashlight about 1 cm from the pinhole. The pinhole screen should be about 50 cm from the projection screen, as shown in the diagram. Adjust the distance to form a sharp image on the projection screen.



Discussion

1. Did you observe interference patterns on the screen?
2. As a result of your observations, what do you conclude about the nature of light?

Solutions to the Schrödinger wave equation are known as wave functions. Based on the Heisenberg uncertainty principle, the early developers of quantum theory determined that wave functions give only the *probability* of finding an electron at a given place around the nucleus. Thus, electrons do not travel around the nucleus in neat orbits, as Bohr had postulated. Instead, they exist in certain regions called orbitals. *An* **orbital** *is a three-dimensional region around the nucleus that indicates the probable location of an electron.*

Figure 4-11 illustrates two ways of picturing one type of atomic orbital. As you will see later in this section, atomic orbitals have different shapes and sizes.

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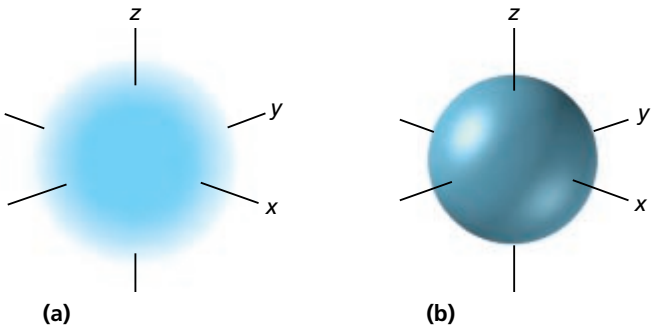

FIGURE 4-11 Two ways of showing a simple atomic orbital are presented. In (a) the probability of finding the electron is proportional to the density of the cloud. Shown in (b) is a surface within which the electron can be found a certain percentage of the time, in this case 90%.

Atomic Orbitals and Quantum Numbers

In the Bohr atomic model, electrons of increasing energy occupy orbits farther and farther from the nucleus. According to the Schrödinger equation, electrons in atomic orbitals also have quantized energies. An electron's energy level is not the only characteristic of an orbital that is indicated by solving the Schrödinger equation.

In order to completely describe orbitals, scientists use quantum numbers. **Quantum numbers** *specify the properties of atomic orbitals and the properties of electrons in orbitals*. The first three quantum numbers result from solutions to the Schrödinger equation. They indicate the main energy level, the shape, and the orientation of an orbital. The fourth, the spin quantum number, describes a fundamental state of the electron that occupies the orbital. As you read the following descriptions of the quantum numbers, refer to the appropriate columns in Table 4-2 on page 104.

Principal Quantum Number

The **principal quantum number,** *symbolized by n, indicates the main energy level occupied by the electron.* Values of n are positive integers only—1, 2, 3, and so on. As n increases, the electron's energy and its average distance from the nucleus increase (see Figure 4-12). For example, an electron for which $n = 1$ occupies the first, or lowest, main energy level and is located closest to the nucleus. As you will see, more than one electron can have the same n value. These electrons are sometimes said to be in the same electron *shell.* The total number of orbitals that exist in a given shell, or main energy level, is equal to n^2.

Angular Momentum Quantum Number

Except at the first main energy level, orbitals of different shapes—known as *sublevels*—exist for a given value of n. *The* **angular momentum quantum number,** *symbolized by l, indicates the shape of the orbital.* For a specific main energy level, the number of orbital shapes possible is equal to n. The values of l allowed are zero and all positive integers less

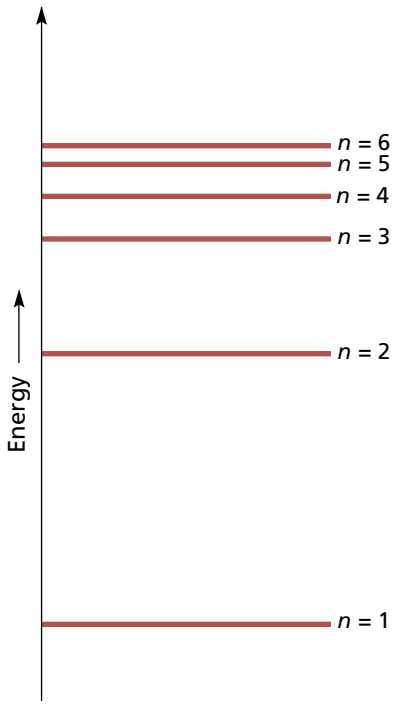

FIGURE 4-12 The main energy levels of an atom are represented by the principal quantum number, n.

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TABLE 4-1 Orbital Letter Designations According to Values of *l*

l	Letter
0	*s*
1	*p*
2	*d*
3	*f*

than or equal to $n - 1$. For example, orbitals for which $n = 2$ can have one of two shapes corresponding to $l = 0$ and $l = 1$. Depending on its value of l, an orbital is assigned a letter, as shown in Table 4-1.

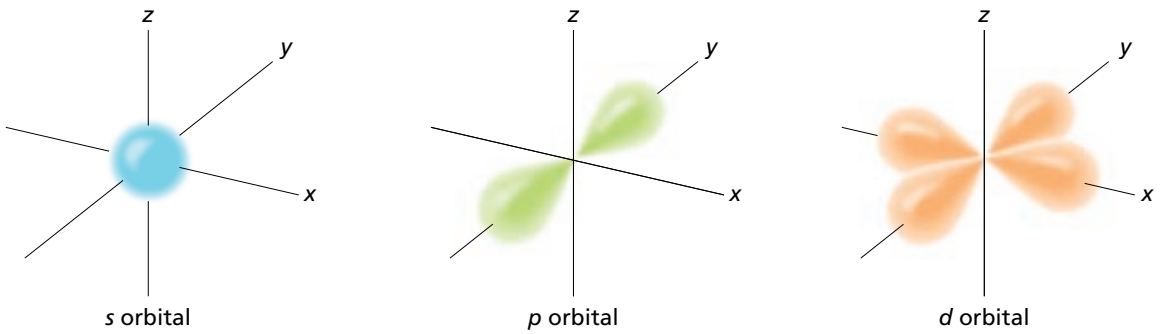
As shown in Figure 4-13, *s* orbitals are spherical, *p* orbitals have dumbbell shapes, and *d* orbitals are more complex. (The *f* orbital shapes are too complex to discuss here.) In the first energy level, $n = 1$, there is only one sublevel possible—an *s* orbital. As mentioned, the second energy level, $n = 2$, has two sublevels—the *s* and *p* orbitals. The third energy level, $n = 3$, has three sublevels—the *s*, *p*, and *d* orbitals. The fourth energy level, $n = 4$, has four sublevels—the *s*, *p*, *d*, and *f* orbitals. In an *n*th main energy level, there are *n* sublevels.

Each atomic orbital is designated by the principal quantum number followed by the letter of the sublevel. For example, the 1*s* sublevel is the *s* orbital in the first main energy level, while the 2*p* sublevel is the set of *p* orbitals in the second main energy level. On the other hand, a 4*d* orbital is part of the *d* sublevel in the fourth main energy level. How would you designate the *p* sublevel in the third main energy level? How many other sublevels are in the same main energy level with this one?

Magnetic Quantum Number

Atomic orbitals can have the same shape but different orientations around the nucleus. *The* **magnetic quantum number,** *symbolized by m, indicates the orientation of an orbital around the nucleus.* Here we describe the orbital orientations that correspond to various values of *m*. Because an *s* orbital is spherical and is centered around the nucleus, it has only one possible orientation. This orientation corresponds to a

FIGURE 4-13 The orbitals *s*, *p*, and *d* have different shapes. Each of the orbitals shown occupies a different region of space around the nucleus.



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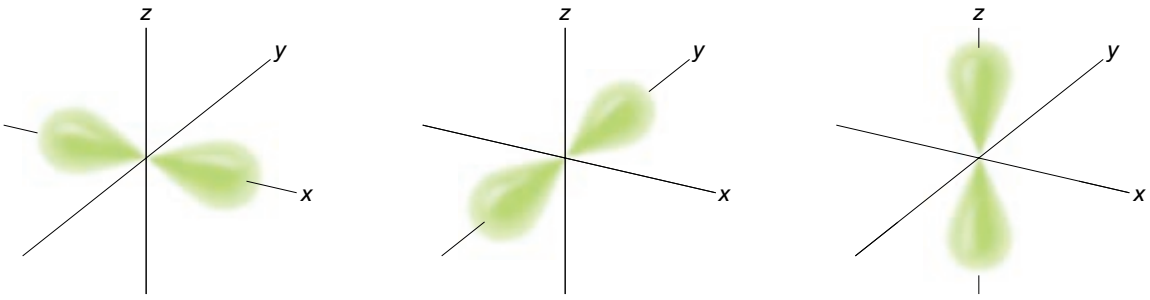

FIGURE 4-14 The subscripts *x*, *y*, and *z* indicate the three different orientations of *p* orbitals. The intersection of the *x*, *y*, and *z* axes indicates the location of the center of the nucleus.

magnetic quantum number of $m = 0$. There is therefore only one *s* orbital in each *s* sublevel. As shown in Figure 4-14, the lobes of a *p* orbital can extend along the *x*, *y*, or *z* axis of a three-dimensional coordinate system. There are therefore three *p* orbitals in each *p* sublevel, which are designated as p_x, p_y, and p_z orbitals. The three *p* orbitals occupy different regions of space and correspond, in no particular order, to values of $m = -1$, $m = 0$, and $m = +1$.

There are five different *d* orbitals in each *d* sublevel (see Figure 4-15). The five different orientations, including one with a different shape, correspond to values of $m = -2$, $m = -1$, $m = 0$, $m = +1$, and $m = +2$. There are seven different *f* orbitals in each *f* sublevel.

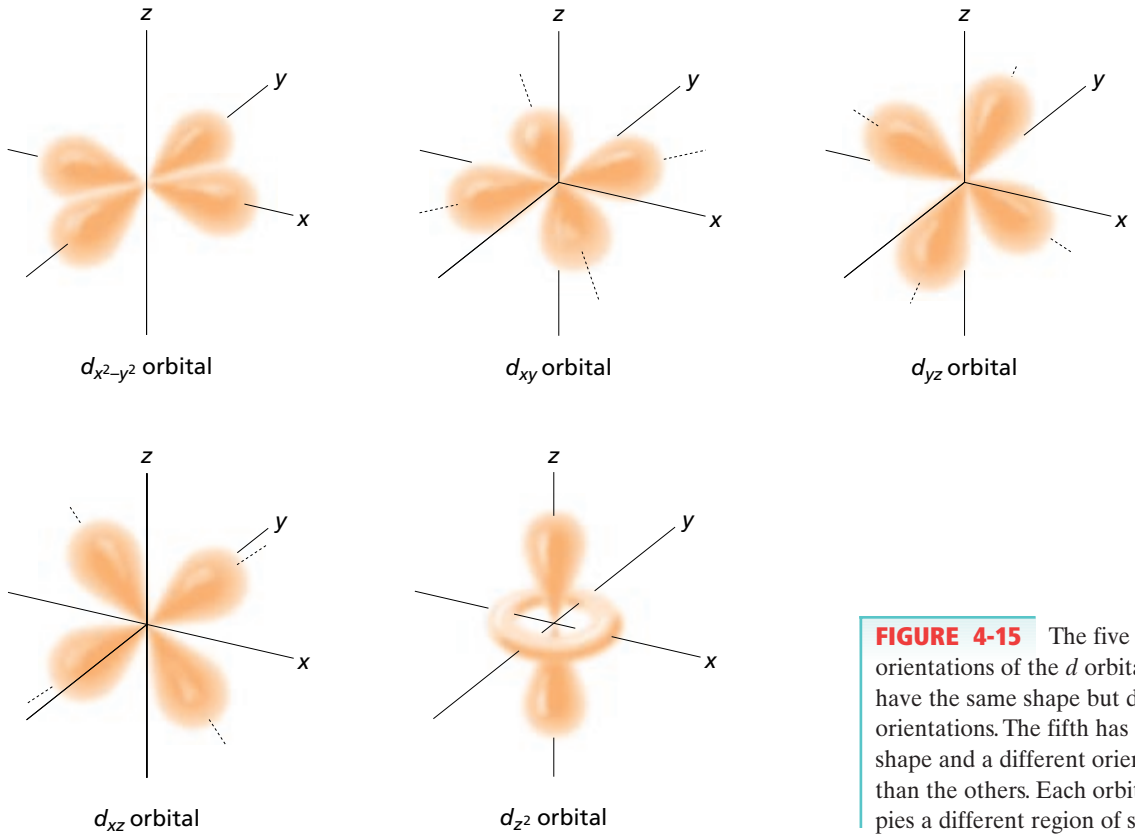

FIGURE 4-15 The five different orientations of the *d* orbitals. Four have the same shape but different orientations. The fifth has a different shape and a different orientation than the others. Each orbital occupies a different region of space.

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TABLE 4-2 *Quantum Number Relationships in Atomic Structure*

Principal quantum number: main energy level (n)	Sublevels in main energy level (n sublevels)	Number of orbitals per sublevel	Number of orbitals per main energy level (n^2)	Number of electrons per sublevel	Number of electrons per main energy level ($2n^2$)
1	s	1	1	2	2
2	s p	1 3	4	2 6	8
3	s p d	1 3 5	9	2 6 10	18
4	s p d f	1 3 5 7	16	2 6 10 14	32

As you can see in Table 4-2, the total number of orbitals at a main energy level increases with the value of n. In fact, the number of orbitals at each main energy level equals the square of the principal quantum number, n^2. What is the total number of orbitals in the third energy level? Specify each of the sublevels using the three quantum numbers you've learned so far.

Spin Quantum Number

Like Earth, an electron in an orbital can be thought of as spinning on an internal axis. It spins in one of two possible directions, or states. As it spins, it creates a magnetic field. To account for the magnetic properties of the electron, theoreticians of the early twentieth century created the spin quantum number. *The* **spin quantum number** *has only two possible values—(+½, −½)—which indicate the two fundamental spin states of an electron in an orbital.* A single orbital can hold a maximum of two electrons, which must have opposite spins.

SECTION REVIEW

1. Define the following:
   a. main energy levels
   b. quantum numbers
2. a. List the four quantum numbers.
   b. What general information about atomic orbitals is provided by the quantum numbers?
3. Describe briefly what specific information is given by each of the four quantum numbers.

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Electron Configurations

SECTION 4-3

Objectives

- List the total number of electrons needed to fully occupy each main energy level.
- State the Aufbau principle, the Pauli exclusion principle, and Hund's rule.
- Describe the electron configurations for the atoms of any element using orbital notation, electron-configuration notation, and, when appropriate, noble-gas notation.

The quantum model of the atom improves on the Bohr model because it describes the arrangements of electrons in atoms other than hydrogen. *The arrangement of electrons in an atom is known as the atom's* **electron configuration.** Because atoms of different elements have different numbers of electrons, a distinct electron configuration exists for the atoms of each element. Like all systems in nature, electrons in atoms tend to assume arrangements that have the lowest possible energies. The lowest-energy arrangement of the electrons for each element is called the element's *ground-state electron configuration.* A few simple rules, combined with the quantum number relationships discussed in Section 4-2, allow us to determine these ground-state electron configurations.

Rules Governing Electron Configurations

To build up electron configurations for the ground state of any particular atom, first the energy levels of the orbitals are determined. Then electrons are added to the orbitals one by one according to three basic rules. (Remember that real atoms are not built up by adding protons and electrons one at a time.)

The first rule shows the order in which electrons occupy orbitals. According to the **Aufbau principle,** *an electron occupies the lowest-energy orbital that can receive it.* Figure 4-16 shows the atomic orbitals in order of increasing energy. The orbital with the lowest energy is the 1*s* orbital. In a ground-state hydrogen atom, the electron is in this orbital. The 2*s* orbital is the next highest in energy, then the 2*p* orbitals. Beginning with the third main energy level, $n = 3$, the energies of the sublevels in different main energy levels begin to overlap.

Note in the figure, for example, that the 4*s* sublevel is lower in energy than the 3*d* sublevel. Therefore, the 4*s* orbital is filled before any electrons enter the 3*d* orbitals. (Less energy is required for two electrons to pair up in the 4*s* orbital than for a single electron to

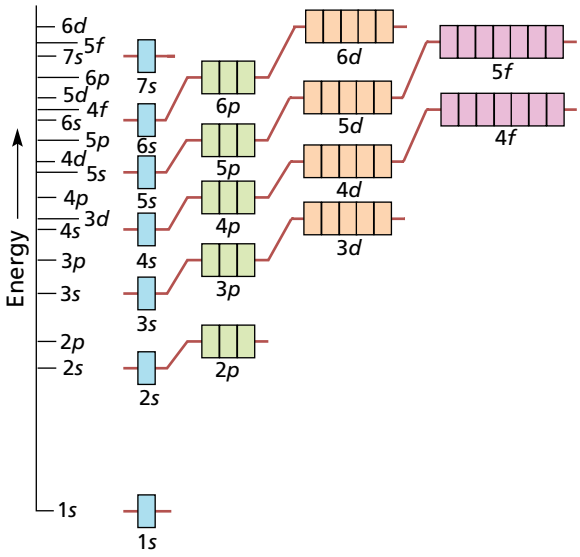

FIGURE 4-16 The order of increasing energy for atomic sublevels is shown on the vertical axis. Each individual box represents an orbital.

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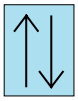


1*s* orbital

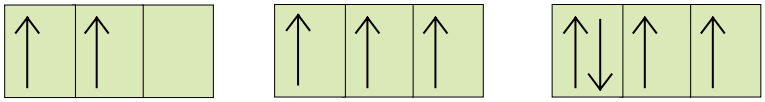
FIGURE 4-17 According to the Pauli exclusion principle, an orbital can hold two electrons of opposite spin. In this electron configuration of a helium atom, each arrow represents one of the atom's two electrons. The direction of the arrow indicates the electron's spin.

occupy a 3*d* orbital.) Once the 3*d* orbitals are fully occupied, which sublevel will be occupied next?

The second rule reflects the importance of the spin quantum number. According to the **Pauli exclusion principle,** *no two electrons in the same atom can have the same set of four quantum numbers.* The principal, angular momentum, and magnetic quantum numbers specify the energy, shape, and orientation of an orbital. The two values of the spin quantum number allow two electrons of opposite spins to occupy the orbital (see Figure 4-17).

The third rule requires placing as many unpaired electrons as possible in separate orbitals in the same sublevel. In this way, electron-electron repulsion is minimized so that the electron arrangements have the lowest energy possible. According to **Hund's rule,** *orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin.* Applying this rule shows, for example, that one electron will enter each of the three *p* orbitals in a main energy level before a second electron enters any of them. This is illustrated in Figure 4-18. What is the maximum number of unpaired electrons in a *d* sublevel?

FIGURE 4-18 The figure shows how (a) two, (b) three, and (c) four electrons fill the *p* sublevel of a given main energy level according to Hund's rule.



(a) (b) (c)

Representing Electron Configurations

Three methods, or notations, are used to indicate electron configurations. Two of these notations will be discussed in the next two sections for the first-period elements, hydrogen and helium. The third notation applies mostly to elements of the third period and higher. It will be discussed in the section on third-period elements.

In a ground-state hydrogen atom, the single electron is in the lowest-energy orbital, the 1*s* orbital. The electron can be in either one of its two spin states. Helium has two electrons, which are paired in the 1*s* orbital.

Orbital Notation

In orbital notation, an unoccupied orbital is represented by a line, ___, with the orbital's name written underneath the line. An orbital containing one electron is represented as ↑ . An orbital containing two electrons is represented as ↑↓ , showing the electrons paired and with opposite spins. The lines are labeled with the principal quantum number

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and sublevel letter. For example, the orbital notations for hydrogen and helium are written as follows.

$$\text{H}\ \frac{\uparrow}{1s} \qquad \text{He}\ \frac{\uparrow\downarrow}{1s}$$

Electron-Configuration Notation

Electron-configuration notation eliminates the lines and arrows of orbital notation. Instead, the number of electrons in a sublevel is shown by adding a superscript to the sublevel designation. The hydrogen configuration is represented by $1s^1$. The superscript indicates that one electron is present in hydrogen's 1*s* orbital. The helium configuration is represented by $1s^2$. Here the superscript indicates that there are two electrons in helium's 1*s* orbital.

SAMPLE PROBLEM 4-1

The electron configuration of boron is $1s^2 2s^2 2p^1$. How many electrons are present in an atom of boron? What is the atomic number for boron? Write the orbital notation for boron.

SOLUTION

The number of electrons in a boron atom is equal to the sum of the superscripts in its electron-configuration notation: 2 + 2 + 1 = 5 electrons. The number of protons equals the number of electrons in a neutral atom. So we know that boron has 5 protons and thus has an atomic number of 5. To write the orbital notation, first draw the lines representing orbitals.

$$\underline{1s}\quad\underline{2s}\quad\underline{2p_x}\ \underline{2p_y}\ \underline{2p_z}$$

Next, add arrows showing the electron locations. The first two electrons occupy $n = 1$ energy level and fill the 1*s* orbital.

$$\frac{\uparrow\downarrow}{1s}\quad\underline{2s}\quad\underline{2p_x}\ \underline{2p_y}\ \underline{2p_z}$$

The next three electrons occupy the $n = 2$ main energy level. According to the Aufbau principle, two of these occupy the lower-energy 2*s* orbital. The third occupies a higher-energy *p* orbital.

$$\frac{\uparrow\downarrow}{1s}\ \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p_x}\ \underline{2p_y}\ \underline{2p_z}$$

PRACTICE

1. The electron configuration of nitrogen is $1s^2 2s^2 2p^3$. How many electrons are present in a nitrogen atom? What is the atomic number of nitrogen? Write the orbital notation for nitrogen.

Answer

7, 7, $\frac{\uparrow\downarrow}{1s}\ \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p_x}\ \frac{\uparrow}{2p_y}\ \frac{\uparrow}{2p_z}$

2. The electron configuration of fluorine is $1s^2 2s^2 2p^5$. What is the atomic number of fluorine? How many of its *p* orbitals are filled? How many unpaired electrons does a fluorine atom contain?

Answer

9, 2, 1

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The Noble Decade

HISTORICAL PERSPECTIVE

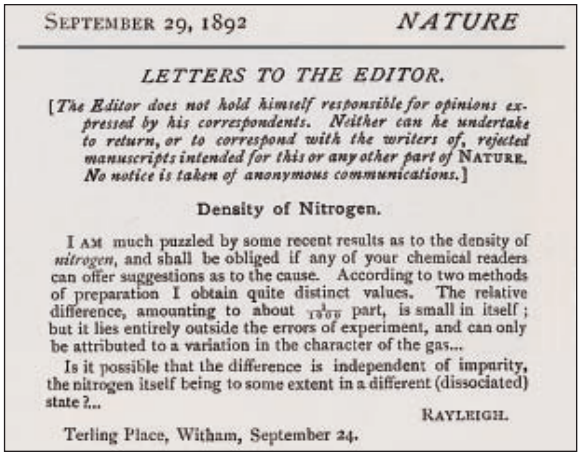
By the late nineteenth century, the science of chemistry had begun to be organized. The first international congress of chemistry, in 1860, established the field's first standards. And Dmitri Mendeleev's periodic table of elements gave chemists across the globe a systematic understanding of matter's building blocks. But many important findings were yet to come, including the discovery of a family of rare, unreactive gases that were unlike any substances known at the time.

Cross-Disciplinary Correspondence

In 1888, the British physicist Lord Rayleigh encountered a small but significant discrepancy in the results of one of his experiments. In an effort to redetermine the atomic mass of nitrogen, he measured the densities of several samples of nitrogen gas. Each sample had been prepared by a different method. The samples that had been isolated from chemical reactions all exhibited similar densities. But they were about one-tenth of a percent lighter than the nitrogen isolated from air, which at the time was believed to be a mixture of nitrogen, oxygen, water vapor, and carbon dioxide.

Rayleigh was at a loss to explain his discovery. Finally, in 1892, he published a letter in *Nature* magazine appealing to his colleagues for an explanation. A month later he received a reply from a Scottish chemist named William Ramsay. Ramsay related that he too had been stumped by the density difference between chemical and atmospheric nitrogen. Rayleigh decided to report his findings to the Royal Society of Chemistry, adding:

> *Until the questions arising out of these observations are thoroughly cleared up, the above number [density] for nitrogen must be received with a certain reserve.*



SEPTEMBER 29, 1892 NATURE

LETTERS TO THE EDITOR.

[*The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, or to correspond with the writers of, rejected manuscripts intended for this or any other part of* NATURE. *No notice is taken of anonymous communications.*]

Density of Nitrogen.

I AM much puzzled by some recent results as to the density of *nitrogen*, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to two methods of preparation I obtain quite distinct values. The relative difference, amounting to about $\frac{1}{100}$ part, is small in itself; but it lies entirely outside the errors of experiment, and can only be attributed to a variation in the character of the gas...

Is it possible that the difference is independent of impurity, the nitrogen itself being to some extent in a different (dissociated) state?...

RAYLEIGH.

Terling Place, Witham, September 24.

An excerpt of Lord Rayleigh's letter as originally published in Nature *magazine in 1892*

A Chemist's Approach

With Rayleigh's permission, Ramsay attempted to remove all the known components from a sample of air and analyze what, if anything, remained. First he heated magnesium in the air to remove all of the nitrogen in the form of magnesium nitride. Then he removed the oxygen, water vapor, and carbon dioxide factions. What remained was a minuscule portion of a mysterious gas.

Ramsay tried to cause the gas to react with chemically active substances, such as hydrogen, sodium, and caustic soda, but the gas remained unaltered. He decided to name this new atmospheric component argon (Greek for "inert" or "idle"):

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TOPIC: William Ramsay
GO TO: www.scilinks.org
***sci*LINKS CODE:** HC2043

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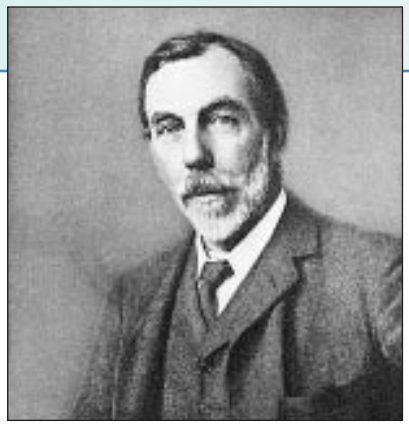

In 1893, Scottish chemist William Ramsay isolated a previously unknown component of the atmosphere.

> *The gas deserves the name "argon," for it is a most astonishingly indifferent body. . . .*

Periodic Problems

Rayleigh and Ramsay were sure that they had discovered a new element. But this created a problem. Their calculations indicated that argon had an atomic mass of about 40. However, there was no space in the periodic table as it appeared in 1894 for such an element. The elements with atomic masses closest to that of argon were chlorine and potassium. Unfortunately, the chemical properties of the families of each of these elements were completely dissimilar to those of the strange gas.

Ramsay contemplated argon's lack of reactivity. He knew that Mendeleev had created the periodic table on the basis of valence, or the number of atomic partners an element bonds with in forming a compound. As Ramsay could not cause argon to form any compounds, he assigned it a valence of zero. And because the valence of the elements in the families of both chlorine and potassium was one, perhaps argon fit in between them. In May 1894, Ramsay wrote to Rayleigh:

> *Has it occurred to you that there is room for gaseous elements at the end of the first column of the periodic table?…Such elements should have the density 20 or thereabouts, and 0.8 pc [percent] (1/120th about) of the nitrogen of the air could so raise the density of nitrogen that it would stand to pure [chemical] nitrogen in the ratio of 230:231.*

Ramsay's insight that argon merited a new spot in the periodic table, between the chlorine family and the potassium family, was correct. And, as he would soon confirm, his newly discovered gas was indeed one of a previously unknown family of elements.

New Neighbors

In 1895, Ramsay isolated a light, inert gas from a mineral called cleveite. Physical analysis revealed that the gas was the same as one that had been identified in the sun in 1868—helium. Helium was the second zero-valent element found on Earth, and its discovery made chemists aware that the periodic table had been missing a whole column of elements.

Over the next three years, Ramsay and his assistant, Morris Travers, identified three more inert gases present in the atmosphere: neon (Greek for "new"), krypton ("hidden"), and xenon ("stranger"). Finally in 1900, German chemist Friedrich Ernst Dorn discovered radon, the last of the new family of elements known today as the noble gases. For his discovery, Ramsay received the Nobel Prize in 1904.

Groups / Periods	III b	IV b	V b	VI b	VII b	VIII b	I b	II b	III a	IV a	V a	VI a	VII a	0	I a	II a
1															H	He
2															Li	Be
3									B	C	N	O	F	Ne	Na	Mg
4									Al	Si	P	S	Cl	Ar	K	Ca
5	Sc	Ti	V	Cr	Mn	Fe Co Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr
6	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba
7	La	Hf	Ta	W	Re	Os Ir Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra
8	Ac															
	Transition elements								Main-group elements							

One version of the periodic table as it appeared after the discovery of the noble gases. The placement of the Group 1 and 2 elements at the far right of the table shows clearly how the noble gases fit in between the chlorine family and the potassium family of elements. The "0" above the noble-gas family indicates the zero valency of the gases.

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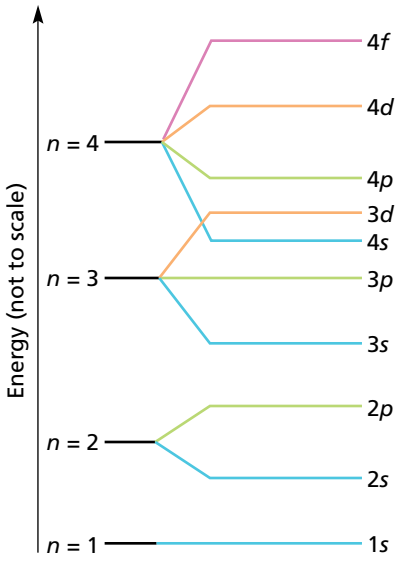

FIGURE 4-19 The direction of the arrow indicates the order in which atomic orbitals are filled according to the Aufbau principle.

Elements of the Second Period

In the first-period elements, hydrogen and helium, electrons occupy the first main energy level. The ground-state configurations in Table 4-3 illustrate how the Aufbau principle, the Pauli exclusion principle, and Hund's rule are applied to atoms of elements in the second period. Figure 4-19 shows the first four main energy levels in order of increasing energy for applying the Aufbau principle.

According to the Aufbau principle, after the 1*s* orbital is filled, the next electron occupies the *s* sublevel in the second main energy level. Thus, lithium, Li, has a configuration of $1s^2 2s^1$. The electron occupying the 2*s* level of a lithium atom is in the atom's highest, or outermost, occupied level. *The* **highest occupied level** *is the electron-containing main energy level with the highest principal quantum number.* The two electrons in the 1*s* sublevel of lithium are no longer in the outermost main energy level. They have become **inner-shell electrons,** *which are electrons that are not in the highest occupied energy level.*

The fourth electron in an atom of beryllium, Be, must complete the pair in the 2*s* sublevel because this sublevel is of lower energy than the 2*p* sublevel. With the 2*s* sublevel filled, the 2*p* sublevel, which has three vacant orbitals of equal energy, can be occupied. Hund's rule applies here, as is shown in the orbital notations in Table 4-3. One of the three *p* orbitals is occupied by a single electron in an atom of boron, B. Two of the three *p* orbitals are occupied by unpaired electrons in an atom of carbon, C. And all three *p* orbitals are occupied by unpaired electrons in an atom of nitrogen, N.

According to the Aufbau principle, the next electron must pair with another electron in one of the 2*p* orbitals rather than enter the third main energy level. The Pauli exclusion principle allows the electron to pair with

TABLE 4-3 ***Electron Configurations of Atoms of Second-Period Elements Showing Two Notations***

Name	Symbol	Orbital notation 1*s*	2*s*	2*p*			Electron-configuration notation
Lithium	Li	↑↓	↑				$1s^2 2s^1$
Beryllium	Be	↑↓	↑↓				$1s^2 2s^2$
Boron	B	↑↓	↑↓	↑			$1s^2 2s^2 2p^1$
Carbon	C	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^2$
Nitrogen	N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$
Oxygen	O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$
Fluorine	F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$
Neon	Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$

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one of the electrons occupying the 2*p* orbitals as long as the spins of the paired electrons are opposite. Thus, atoms of oxygen, O, have the configuration $1s^2 2s^2 2p^4$. Oxygen's orbital notation is shown in Table 4-3.

Two 2*p* orbitals are filled in fluorine, F, and all three are filled in neon, Ne. Atoms such as those of neon, which have the *s* and *p* sublevels of their highest occupied level filled with eight electrons, are said to have an *octet* of electrons. Examine the periodic table inside the back cover of the text. Notice that neon is the last element in the second period.

Elements of the Third Period

After the outer octet is filled in neon, the next electron enters the *s* sublevel in the $n = 3$ main energy level. Thus, atoms of sodium, Na, have the configuration $1s^2 2s^2 2p^6 3s^1$. Compare the configuration of a sodium atom with that of an atom of neon in Table 4-3. Notice that the first 10 electrons in a sodium atom have the same configuration as a neon atom, $1s^2 2s^2 2p^6$. In fact, the first 10 electrons in an atom of each of the third-period elements have the same configuration as neon. This similarity allows us to use a shorthand notation for the electron configurations of the third-period elements.

Noble-Gas Notation

Neon is a member of the Group 18 elements. *The Group 18 elements (helium, neon, argon, krypton, xenon, and radon) are called the* **noble gases.** To simplify sodium's notation, the symbol for neon, enclosed in square brackets, is used to represent the complete neon configuration: $[\text{Ne}] = 1s^2 2s^2 2p^6$. This allows us to write sodium's electron configuration as $[\text{Ne}]3s^1$, which is called sodium's *noble-gas notation.* Table 4-4 shows the noble-gas notation of the electron configuration of each of the third-period elements.

TABLE 4-4 *Electron Configurations of Atoms of Third-Period Elements*

Name	Symbol	Atomic number	Number of electrons in sublevels					Noble-gas notation
			1*s*	2*s*	2*p*	3*s*	3*p*	
Sodium	Na	11	2	2	6	1		$[\text{Ne}]3s^1$
Magnesium	Mg	12	2	2	6	2		$[\text{Ne}]3s^2$
Aluminum	Al	13	2	2	6	2	1	$[\text{Ne}]3s^2 3p^1$
Silicon	Si	14	2	2	6	2	2	$[\text{Ne}]3s^2 3p^2$
Phosphorus	P	15	2	2	6	2	3	$[\text{Ne}]3s^2 3p^3$
Sulfur	S	16	2	2	6	2	4	$[\text{Ne}]3s^2 3p^4$
Chlorine	Cl	17	2	2	6	2	5	$[\text{Ne}]3s^2 3p^5$
Argon	Ar	18	2	2	6	2	6	$[\text{Ne}]3s^2 3p^6$

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The last element in the third period is argon, Ar, which is a noble gas. As in neon, the highest-occupied energy level of argon has an octet of electrons, $[Ne]3s^2 3p^6$. In fact, each noble gas other than He has an electron octet in its highest energy level. *A* **noble-gas configuration** *is an outer main energy level fully occupied, in most cases, by eight electrons.*

Elements of the Fourth Period

The electron configurations of atoms in the fourth-period elements are shown in Table 4-5. The period begins by filling the 4*s* orbital, the empty orbital of lowest energy. Thus, the first element in the fourth period is potassium, K, which has the electron configuration $[Ar]4s^1$. The next element is calcium, Ca, which has the electron configuration $[Ar]4s^2$.

With the 4*s* sublevel filled, the 4*p* and 3*d* sublevels are the next available vacant orbitals. Figure 4-19 on page 110 shows that the 3*d* sublevel

TABLE 4-5 *Electron Configuration of Atoms of Elements in the Fourth Period*

Name	Symbol	Atomic number	Number of electrons in sublevels above 2*p*					Noble-gas notation
			3*s*	3*p*	3*d*	4*s*	4*p*	
Potassium	K	19	2	6		1		*$[Ar]4s^1$
Calcium	Ca	20	2	6		2		$[Ar]4s^2$
Scandium	Sc	21	2	6	1	2		$[Ar]3d^1 4s^2$
Titanium	Ti	22	2	6	2	2		$[Ar]3d^2 4s^2$
Vanadium	V	23	2	6	3	2		$[Ar]3d^3 4s^2$
Chromium	Cr	24	2	6	5	1		$[Ar]3d^5 4s^1$
Manganese	Mn	25	2	6	5	2		$[Ar]3d^5 4s^2$
Iron	Fe	26	2	6	6	2		$[Ar]3d^6 4s^2$
Cobalt	Co	27	2	6	7	2		$[Ar]3d^7 4s^2$
Nickel	Ni	28	2	6	8	2		$[Ar]3d^8 4s^2$
Copper	Cu	29	2	6	10	1		$[Ar]3d^{10} 4s^1$
Zinc	Zn	30	2	6	10	2		$[Ar]3d^{10} 4s^2$
Gallium	Ga	31	2	6	10	2	1	$[Ar]3d^{10} 4s^2 4p^1$
Germanium	Ge	32	2	6	10	2	2	$[Ar]3d^{10} 4s^2 4p^2$
Arsenic	As	33	2	6	10	2	3	$[Ar]3d^{10} 4s^2 4p^3$
Selenium	Se	34	2	6	10	2	4	$[Ar]3d^{10} 4s^2 4p^4$
Bromine	Br	35	2	6	10	2	5	$[Ar]3d^{10} 4s^2 4p^5$
Krypton	Kr	36	2	6	10	2	6	$[Ar]3d^{10} 4s^2 4p^6$

*$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

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is lower in energy than the 4*p* sublevel. Therefore, the five 3*d* orbitals are next to be filled. A total of 10 electrons can occupy the 3*d* orbitals. These are filled successively in the 10 elements from scandium (atomic number 21) to zinc (atomic number 30).

Scandium, Sc, has the electron configuration $[Ar]3d^1 4s^2$. Titanium, Ti, has the configuration $[Ar]3d^2 4s^2$. And vanadium, V, has the configuration $[Ar]3d^3 4s^2$. Up to this point, three electrons with the same spin have been added to three separate *d* orbitals, as required by Hund's rule.

Surprisingly, chromium, Cr, has the electron configuration $[Ar]3d^5 4s^1$. Not only did the added electron go into the fourth 3*d* orbital, but an electron also moved from the 4*s* orbital into the fifth 3*d* orbital, leaving the 4*s* orbital with a single electron. Chromium's electron configuration is contrary to what is expected according to the Aufbau principle. However, in reality the $[Ar]3d^5 4s^1$ configuration is of lower energy than a $[Ar]3d^4 4s^2$ configuration. For chromium, having six outer orbitals with unpaired electrons is a more stable arrangement than having four unpaired electrons in the 3*d* orbitals and forcing two electrons to pair up in the 4*s* orbital. On the other hand, for tungsten, W, which is in the same group as chromium, having four electrons in the 5*d* orbitals and two electrons paired in the 6*s* orbital is the most stable arrrangement. Unfortunately, there is no simple explanation for such deviations from the ideal order given in Figure 4-19.

Manganese, Mn, has the electron configuration $[Ar]3d^5 4s^2$. The added electron goes to the 4*s* orbital, completely filling this orbital while leaving the 3*d* orbitals still half-filled. Beginning with the next element, electrons continue to pair in the *d* orbitals. Thus, iron, Fe, has the configuration $[Ar]3d^6 4s^2$; cobalt, Co, has the configuration $[Ar]3d^7 4s^2$; and nickel, Ni, has the configuration $[Ar]3d^8 4s^2$. Next is copper, Cu, in which an electron moves from the 4*s* orbital to pair with the electron in the fifth 3*d* orbital. The result is an electron configuration of $[Ar]3d^{10} 4s^1$—the lowest-energy configuration for Cu.

In atoms of zinc, Zn, the 4*s* sublevel is filled to give the electron configuration $[Ar]3d^{10} 4s^2$. In atoms of the next six elements, electrons add one by one to the three 4*p* orbitals. According to Hund's rule, one electron is added to each of the three 4*p* orbitals before electrons are paired in any 4*p* orbital.

Elements of the Fifth Period

In the 18 elements of the fifth period, sublevels fill in a similar manner as in elements of the fourth period. However, they start at the 5*s* orbital instead of the 4*s*. Successive electrons are added first to the 5*s* orbital, then to the 4*d* orbitals, and finally to the 5*p* orbitals. This can be seen in Table 4-6 on page 114. There are occasional deviations from the predicted configurations here also. The deviations differ from those for fourth-period elements, but in each case the preferred configuration has the lowest possible energy.

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TABLE 4-6 *Electron Configurations of Atoms of Elements in the Fifth Period*

Name	Symbol	Atomic number	Number of electrons in sublevels above 3*d*					Noble-gas notation
			4*s*	4*p*	4*d*	5*s*	5*p*	
Rubidium	Rb	37	2	6		1		*[Kr]$5s^1$
Strontium	Sr	38	2	6		2		[Kr]$5s^2$
Yttrium	Y	39	2	6	1	2		[Kr]$4d^1 5s^2$
Zirconium	Zr	40	2	6	2	2		[Kr]$4d^2 5s^2$
Niobium	Nb	41	2	6	4	1		[Kr]$4d^4 5s^1$
Molybdenum	Mo	42	2	6	5	1		[Kr]$4d^5 5s^1$
Technetium	Tc	43	2	6	6	1		[Kr]$4d^6 5s^1$
Ruthenium	Ru	44	2	6	7	1		[Kr]$4d^7 5s^1$
Rhodium	Rh	45	2	6	8	1		[Kr]$4d^8 5s^1$
Palladium	Pd	46	2	6	10			[Kr]$4d^{10}$
Silver	Ag	47	2	6	10	1		[Kr]$4d^{10} 5s^1$
Cadmium	Cd	48	2	6	10	2		[Kr]$4d^{10} 5s^2$
Indium	In	49	2	6	10	2	1	[Kr]$4d^{10} 5s^2 5p^1$
Tin	Sn	50	2	6	10	2	2	[Kr]$4d^{10} 5s^2 5p^2$
Antimony	Sb	51	2	6	10	2	3	[Kr]$4d^{10} 5s^2 5p^3$
Tellurium	Te	52	2	6	10	2	4	[Kr]$4d^{10} 5s^2 5p^4$
Iodine	I	53	2	6	10	2	5	[Kr]$4d^{10} 5s^2 5p^5$
Xenon	Xe	54	2	6	10	2	6	[Kr]$4d^{10} 5s^2 5p^6$

*[Kr] = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

SAMPLE PROBLEM 4-2

a. Write both the complete electron-configuration notation and the noble-gas notation for iron, Fe.

b. How many electron-containing orbitals are in an atom of iron? How many of these orbitals are completely filled? How many unpaired electrons are there in an atom of iron? In which sublevel are the unpaired electrons located?

SOLUTION

a. The complete electron-configuration notation of iron is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. The periodic table inside the back cover of the text reveals that $1s^2 2s^2 2p^6 3s^2 3p^6$ is the electron configuration of the noble gas argon, Ar. Therefore, as shown in Table 4-5 on page 112, iron's noble-gas notation is [Ar]$3d^6 4s^2$.

b. An iron atom has 15 orbitals that contain electrons. They consist of one 1s orbital, one 2*s* orbital, three 2*p* orbitals, one 3*s* orbital, three 3*p* orbitals, five 3*d* orbitals, and one 4*s* orbital. Eleven of these orbitals are filled. The notation $3d^6$ represents 3*d* $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$ $\underline{\uparrow}$, so there are four unpaired electrons. They are located in the 3*d* sublevel.

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PRACTICE

1. a. Write both the complete electron-configuration notation and the noble-gas notation for iodine, I. How many inner-shell electrons does an iodine atom contain?

   b. How many electron-containing orbitals are in an atom of iodine? How many of these orbitals are filled? How many unpaired electrons are there in an atom of iodine?

2. a. Write the noble-gas notation for tin, Sn. How many unpaired electrons are there in an atom of tin?

   b. How many electron-containing *d* orbitals are there in an atom of tin? Name the element in the fourth period whose atoms have the same number of highest-energy-level electrons as tin.

3. a. Without consulting the periodic table or a table in this chapter, write the complete electron configuration for the element with atomic number 25.

   b. Identify the element described in item 3a.

Answer

1. a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$, $[Kr]4d^{10}5s^2 5p^5$, 46

   b. 27, 26, 1

2. a. $[Kr]4d^{10}5s^2 5p^2$, 2

   b. 10, germanium

3. a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

   b. manganese

Elements of the Sixth and Seventh Periods

The sixth period consists of 32 elements. It is much longer than the periods that precede it in the periodic table. To build up electron configurations for elements of this period, electrons are added first to the 6*s* orbital in cesium, Cs, and barium, Ba. Then, in lanthanum, La, an electron is added to the 5*d* orbital.

With the next element, cerium, Ce, the 4*f* orbitals begin to fill, giving cerium atoms a configuration of $[Xe]4f^1 5d^1 6s^2$. In the next 13 elements, the 4*f* orbitals are filled. Next the 5*d* orbitals are filled and the period is completed by filling the 6*p* orbitals. Because the 4*f* and the 5*d* orbitals are very close in energy, numerous deviations from the simple rules occur as these orbitals are filled. The electron configurations of the sixth-period elements can be found in the periodic table inside the back cover of the text.

The seventh period is incomplete and consists largely of synthetic elements, which will be discussed in Chapter 22.

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SAMPLE PROBLEM 4-3

a. Write both the complete electron-configuration notation and the noble-gas notation for a rubidium atom.

b. Identify the elements in the second, third, and fourth periods that have the same number of highest-energy-level electrons as rubidium.

SOLUTION

a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$, $[Kr]5s^1$

b. Rubidium has one electron in its highest energy level (the fifth). The elements with the same outermost configuration are, in the second period, lithium, Li; in the third period, sodium, Na; and in the fourth period, potassium, K.

PRACTICE

1. a. Write both the complete electron-configuration notation and the noble-gas notation for a barium atom.

   b. Identify the elements in the second, third, fourth, and fifth periods that have the same number of highest-energy-level electrons as barium.

2. a. Write the noble-gas notation for a gold atom.

   b. Identify the elements in the sixth period that have one unpaired electron in their 6*s* sublevel.

Answer

1. a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$, $[Xe]6s^2$

   b. Be, Mg, Ca, Sr

2. a. $[Xe]4f^{14} 5d^{10} 6s^1$

   b. Au, Cs, Pt

SECTION REVIEW

1. a. What is an atom's electron configuration?
   b. What three principles guide the electron configuration of an atom?
2. What three methods are used to represent the arrangement of electrons in atoms?
3. What is an octet of electrons? Which elements contain an octet of electrons?
4. Write the complete electron-configuration notation, the noble-gas notation, and the orbital notation for the following elements:
   a. carbon b. neon c. sulfur
5. Identify the elements having the following electron configurations:
   a. $1s^2 2s^2 2p^6 3s^2 3p^3$
   b. $[Ar]4s^1$
   c. contains four electrons in its third and outer main energy level
   d. contains one set of paired and three unpaired electrons in its fourth and outer main energy level

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CHAPTER 4 REVIEW

CHAPTER SUMMARY

4-1

- In the early twentieth century, light was determined to have a dual wave-particle nature.
- Quantum theory was developed to explain such observations as the photoelectric effect and the line-emission spectrum of hydrogen.
- Quantum theory states that electrons can exist in atoms only at specific energy levels.
- When an electron moves from one main energy level to a main energy level of lower energy, a photon is emitted. The photon's energy equals the energy difference between the two levels.
- An electron in an atom can move from one main energy level to a higher main energy level only by absorbing an amount of energy exactly equal to the difference between the two levels.

Vocabulary

continuous spectrum (94)
electromagnetic radiation (91)
electromagnetic spectrum (91)
excited state (94)
frequency (92)
ground state (94)
line-emission spectrum (94)
photoelectric effect (93)
photon (94)
quantum (93)
wavelength (91)

4-2

- In the early twentieth century, electrons were determined to have a dual wave-particle nature.
- The Heisenberg uncertainty principle states that it is impossible to determine simultaneously both the position and velocity of an electron or any other particle.
- Quantization of electron energies is a natural outcome of the Schrödinger wave equation, which treats an atom's electrons as waves surrounding the nucleus.
- An orbital is a three-dimensional region around the nucleus that shows the region of probable electron locations.
- The four quantum numbers that describe the properties of electrons in atomic orbitals are the principal quantum number, the angular momentum quantum number, the magnetic quantum number, and the spin quantum number.

Vocabulary

angular momentum quantum number (101)
Heisenberg uncertainty principle (99)
magnetic quantum number (102)
orbital (100)
principal quantum number (101)
quantum numbers (101)
quantum theory (99)
spin quantum number (104)

4-3

- Electrons occupy atomic orbitals in the ground state of an atom according to the Aufbau principle, the Pauli exclusion principle, and Hund's rule.
- Electron configurations can be depicted using different types of notation. In this book, three types of notation are used: orbital notation, electron-configuration notation, and noble-gas notation.
- Electron configurations of some atoms, such as chromium, do not strictly follow the Aufbau principle, but the ground-state configuration that results is the configuration with the minimum possible energy.

Vocabulary

Aufbau principle (105)
electron configuration (105)
highest occupied level (110)
Hund's rule (106)
inner-shell electrons (110)
noble gases (111)
noble-gas configuration (112)
Pauli exclusion principle (106)

REVIEWING CONCEPTS

1. a. List five examples of electromagnetic radiation.
b. What is the speed of all forms of electromagnetic radiation in a vacuum?
c. Relate the frequency and wavelength of any form of electromagnetic radiation. (4-1)

2. Prepare a two-column table. List the properties of light that can best be explained by the wave theory in one column. List those best explained by the particle theory in the second column. You may want to consult a physics textbook for reference. (4-1)

3. What are the frequency and wavelength ranges of visible light? (4-1)

4. List the colors of light in the visible spectrum in order of increasing frequency. (4-1)

5. In the early twentieth century, what two experiments involving light and matter could not be explained by the wave theory of light? (4-1)

6. a. How are the wavelength and frequency of electromagnetic radiation related?
b. How are the energy and frequency of electromagnetic radiation related?
c. How are the energy and wavelength of electromagnetic radiation related? (4-1)

7. Which theory of light, the wave or particle theory, best explains the following phenomena?
a. the interference of light
b. the photoelectric effect
c. the emission of electromagnetic radiation by an excited atom (4-1)

8. Distinguish between the ground state and an excited state of an atom. (4-1)

9. According to the Bohr model of the hydrogen atom, how is hydrogen's emission spectrum produced? (4-1)

10. Describe two major shortcomings of the Bohr model of the atom. (4-2)

11. a. What is the principal quantum number?
b. How is it symbolized?
c. What are shells?
d. How does n relate to the number of orbitals per main energy level and the number of electrons allowed per main energy level? (4-2)

12. a. What information is given by the angular momentum quantum number?
b. What are sublevels, or subshells? (4-2)

13. For each of the following values of n, indicate the numbers and types of sublevels possible for that main energy level. (Hint: See Table 4-2.)
a. $n = 1$
b. $n = 2$
c. $n = 3$
d. $n = 4$
e. $n = 7$ (number only) (4-2)

14. a. What information is given by the magnetic quantum number?
b. How many orbital orientations are possible in each of the *s, p, d,* and *f* sublevels?
c. Explain and illustrate the notation for distinguishing among the different *p* orbitals in a sublevel. (4-2)

15. a. What is the relationship between n and the total number of orbitals in a main energy level?
b. How many total orbitals are contained in the third main energy level? in the fifth? (4-2)

16. a. What information is given by the spin quantum number?
b. What are the possible values for this quantum number? (4-2)

17. How many electrons could be contained in the following main energy levels with n equal to:
a. 1
b. 3
c. 4
d. 6
e. 7 (4-2)

18. a. In your own words, state the Aufbau principle.
b. Explain the meaning of this principle in terms of an atom with many electrons. (4-3)

19. a. In your own words, state Hund's rule.
b. What is the basis for this rule? (4-3)

20. a. In your own words, state the Pauli exclusion principle.
b. What is the significance of the spin quantum number?

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c. Compare the values of the spin quantum number for two electrons in the same orbital. (4-3)

21. a. What is meant by the highest occupied energy level in an atom?
b. What are inner-shell electrons? (4-3)

22. Determine the highest occupied energy level in the following elements:
a. He
b. Be
c. Al
d. Ca
e. Sn (4-3)

23. Write the orbital notation for the following elements. (Hint: See Sample Problem 4-1.)
a. P
b. B
c. Na
d. C (4-3)

24. Write the electron-configuration notation for an unidentified element that contains the following number of electrons:
a. 3
b. 6
c. 8
d. 13 (4-3)

25. Given that the electron configuration for oxygen is $1s^2 2s^2 2p^4$, answer the following questions:
a. How many electrons are in each atom?
b. What is the atomic number of this element?
c. Write the orbital notation for oxygen's electron configuration.
d. How many unpaired electrons does oxygen have?
e. What is the highest occupied energy level?
f. How many inner-shell electrons does the atom contain?
g. In which orbital(s) are these inner-shell electrons located? (4-3)

26. a. What are the noble gases?
b. What is a noble-gas configuration?
c. How does noble-gas notation simplify writing an atom's electron configuration? (4-3)

27. Write the noble-gas notation for the electron configuration of each of the elements that follow. (Hint: See Sample Problem 4-2.)
a. Cl
b. Ca
c. Se (4-3)

28. a. What information is given by the noble-gas notation $[Ne]3s^2$?
b. What element does this represent? (4-3)

29. Write both the complete electron-configuration notation and the noble-gas notation for each of the following elements. (Hint: See Sample Problem 4-3.)
a. Na
b. Sr
c. P (4-3)

30. Identify each of the following atoms on the basis of its electron configuration:
a. $1s^2 2s^2 2p^1$
b. $1s^2 2s^2 2p^5$
c. $[Ne]3s^2$
d. $[Ne]3s^2 3p^2$
e. $[Ne]3s^2 3p^5$
f. $[Ar]4s^1$
g. $[Ar]3d^6 4s^2$ (4-3)

PROBLEMS

Photons and Electromagnetic Radiation

31. Determine the frequency of light with a wavelength of 4.257×10^{-7} cm.

32. Determine the energy in joules of a photon whose frequency is 3.55×10^{17} Hz.

33. Using the two equations $E = h\nu$ and $c = \lambda\nu$, derive an equation expressing E in terms of h, c, and λ.

34. How long would it take a radio wave with a frequency of 7.25×10^5 Hz to travel from Mars to Earth if the distance between the two planets is approximately 8.00×10^7 km?

35. Cobalt-60 ($^{60}_{27}Co$) is an artificial radioisotope that is produced in a nuclear reactor for use as a gamma-ray source in the treatment of certain types of cancer. If the wavelength of the gamma radiation from a cobalt-60 source is 1.00×10^{-3} nm, calculate the energy of a photon of this radiation.

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Orbitals and Electron Configuration

36. List the order in which orbitals generally fill, from the 1*s* to the 7*p* orbital.

37. Write the noble-gas notation for the electron configurations of each of the following elements:
a. As
b. Pb
c. Lr
d. Hg
e. Sn
f. Xe
g. La

38. How do the electron configurations of chromium and copper contradict the Aufbau principle?

MIXED REVIEW

39. a. Which has a longer wavelength, green or yellow light?
b. Which has a higher frequency, an X ray or a microwave?
c. Which travels at a greater speed, ultraviolet or infrared light?

40. Write both the complete electron-configuration and noble-gas notation for each of the following:
a. Ar b. Br c. Al

41. Given the speed of light as 3.0×10^8 m/s, calculate the wavelength of the electromagnetic radiation whose frequency is 7.500×10^{12} Hz.

42. a. What is the electromagnetic spectrum?
b. What units are used to express wavelength?
c. What unit is used to express frequencies of electromagnetic waves?

43. Given that the electron configuration for phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$, answer the following questions:
a. How many electrons are in each atom?
b. What is the atomic number of this element?
c. Write its orbital notation.
d. How many unpaired electrons does an atom of phosphorus have?
e. What is its highest occupied energy level?
f. How many inner-shell electrons does the atom contain?
g. In which orbital(s) are these inner-shell electrons located?

44. What is the frequency of a radio wave with an energy of 1.55×10^{-24} J/photon?

45. Write the noble-gas notation for the electron configurations of each of the following elements:
a. Hf
b. Sc
c. Fe
d. At
e. Ac
f. Zn

46. Describe the major similarities and differences between Schrödinger's model of the atom and the model proposed by Bohr.

47. When sodium is heated, a yellow spectral line whose energy is 3.37×10^{-19} J/photon is produced.
a. What is the frequency of this light?
b. What is its wavelength?

48. a. What is an orbital?
b. Describe an orbital in terms of an electron cloud.

CRITICAL THINKING

49. Inferring Relationships In the emission spectrum of hydrogen shown in Figure 4-5 on page 95, each colored line is produced by the emission of photons with specific energies. Substances also produce absorption spectra when electromagnetic radiation passes through them. Certain wavelengths are absorbed. Using the diagram below, predict what the wavelengths of the absorption lines will be when white light (all the colors of the visible spectrum) is passed through hydrogen gas.

Hydrogen absorption spectrum

50. Applying Models When discussing the photoelectric effect, the minimum energy needed to remove an electron from the metal is called the *work function* and is a characteristic of the metal. For example, chromium, Cr, will emit electrons when the wavelength of the radiation is 284 nm or less. Calculate the work function for chromium. (Hint: You will need to use the two equations that describe the relationships among wavelength, frequency, speed of light, and Planck's constant.)

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TECHNOLOGY & LEARNING

51. Graphing Calculator Calculating Quantum Number Relationships

The graphing calculator can run a program that calculates relationships in atomic structure given the quantum number. Given the principal quantum number 3, you will calculate the number of orbitals, orbital shapes, and electrons. The program will then be used to make the calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. How many oribitals are there given the principle quantum number 12?

b. For the primary quantum number 3, how many possible combinations have a cloverleaf orbital shape (or orbital shape = 0)?

c. Name the total number of electrons for the principle quantum number 4.

HANDBOOK SEARCH

52. Sections 1 and 2 of the *Elements Handbook* (pages 728–739) contain information on an analytical test and a technological application for Group 1 and 2 elements that are based on the emission of light from atoms. Review these sections to answer the following:

a. What analytical technique utilizes the emission of light from excited atoms?

b. What elements in Groups 1 and 2 can be identified by this technique?

c. What types of compounds are used to provide color in fireworks?

d. What wavelengths within the visible spectrum would most likely contain emission lines for barium?

RESEARCH & WRITING

53. Neon signs do not always contain neon gas. The various colored lights produced by the signs are due to the emission of a variety of low-pressure gases in different tubes. Research other kinds of gases used in neon signs and list the colors that they emit.

54. Prepare a report about the photoelectric effect and cite some of its practical uses. Explain the basic operation of each device or technique mentioned.

ALTERNATIVE ASSESSMENT

55. Performance Assessment A spectroscope is a device used to produce and analyze spectra. Construct a simple spectroscope and determine the absorption spectra of several elemental gases. (Your teacher will provide you with the elemental samples.)

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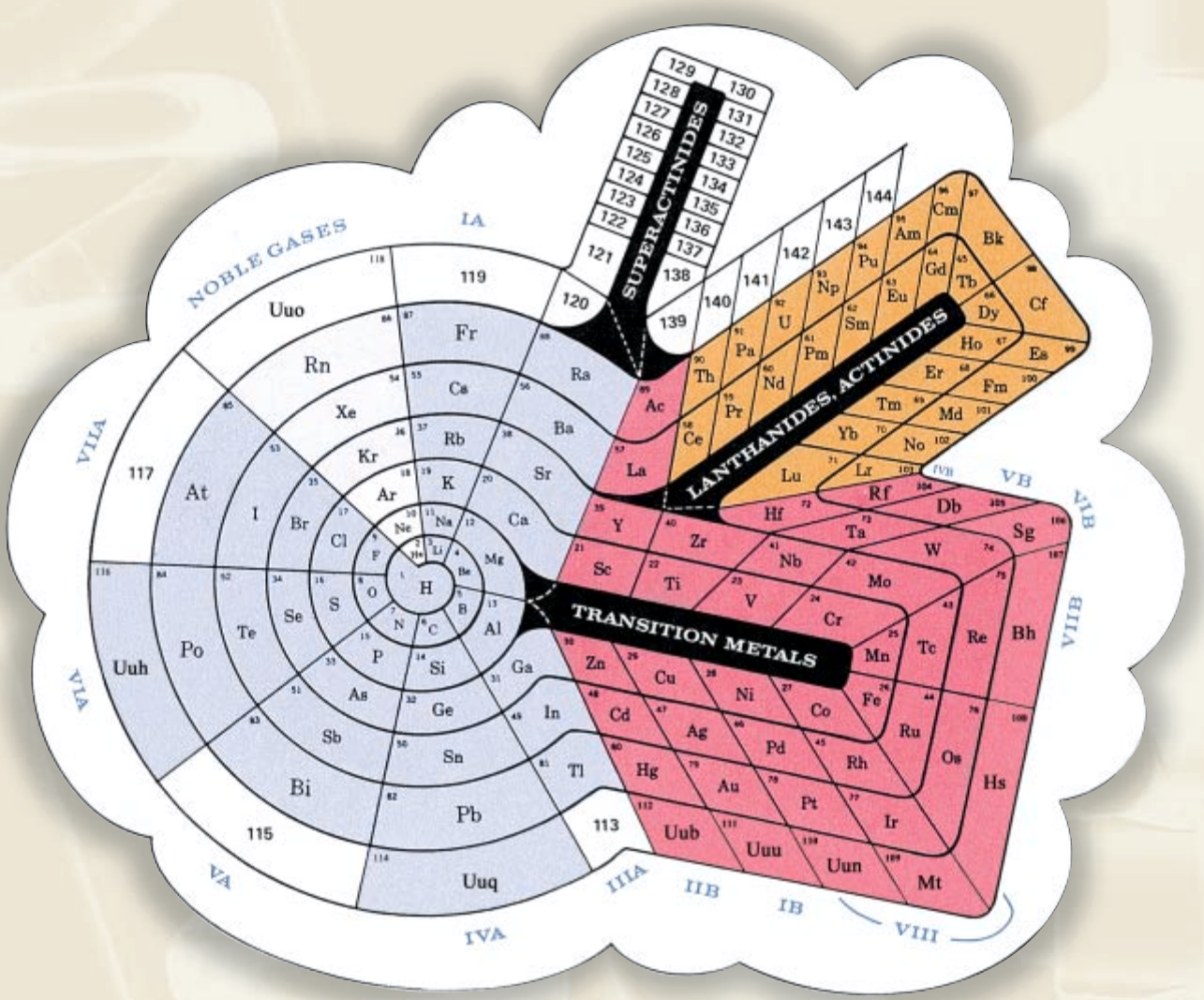
CHAPTER 5

The Periodic Law



The physical and chemical properties of the elements are periodic functions of their atomic numbers.

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History of the Periodic Table

SECTION 5-1

Objectives

- Explain the roles of Mendeleev and Moseley in the development of the periodic table.
- Describe the modern periodic table.
- Explain how the periodic law can be used to predict the physical and chemical properties of elements.
- Describe how the elements belonging to a group of the periodic table are interrelated in terms of atomic number.

Imagine the confusion among chemists during the middle of the nineteenth century. By 1860, more than 60 elements had been discovered. Chemists had to learn the properties of these elements as well as those of the many compounds that they formed—a difficult task. And to make matters worse, there was no method for accurately determining an element's atomic mass or the number of atoms of an element in a particular chemical compound. Different chemists used different atomic masses for the same elements, resulting in different compositions being proposed for the same compounds. This made it nearly impossible for one chemist to understand the results of another.

In September 1860, a group of chemists assembled at the First International Congress of Chemists in Karlsruhe, Germany, to settle the issue of atomic mass as well as some other matters that were making communication difficult. At the Congress, Italian chemist Stanislao Cannizzaro presented a convincing method for accurately measuring the relative masses of atoms. Cannizzaro's method enabled chemists to agree on standard values for atomic mass and initiated a search for relationships between atomic mass and other properties of the elements.

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TOPIC: Periodic table
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Mendeleev and Chemical Periodicity

When the Russian chemist Dmitri Mendeleev heard about the new atomic masses discussed at Karlsruhe, he decided to include the new values in a chemistry textbook that he was writing. In the book, Mendeleev hoped to organize the elements according to their properties. He went about this much as you might organize information for a research paper. He placed the name of each known element on a card, together with the atomic mass of the element and a list of its observed physical and chemical properties. He then arranged the cards according to various properties and looked for trends or patterns.

Mendeleev noticed that when the elements were arranged in order of increasing atomic mass, certain similarities in their chemical properties appeared at regular intervals. Such a repeating pattern is referred to as *periodic*. The second hand of a watch, for example, passes over any given mark at periodic, 60-second intervals. The circular waves created by a drop of water hitting a water surface are also periodic.

FIGURE 5-1 The regularly spaced water waves represent a simple periodic pattern.

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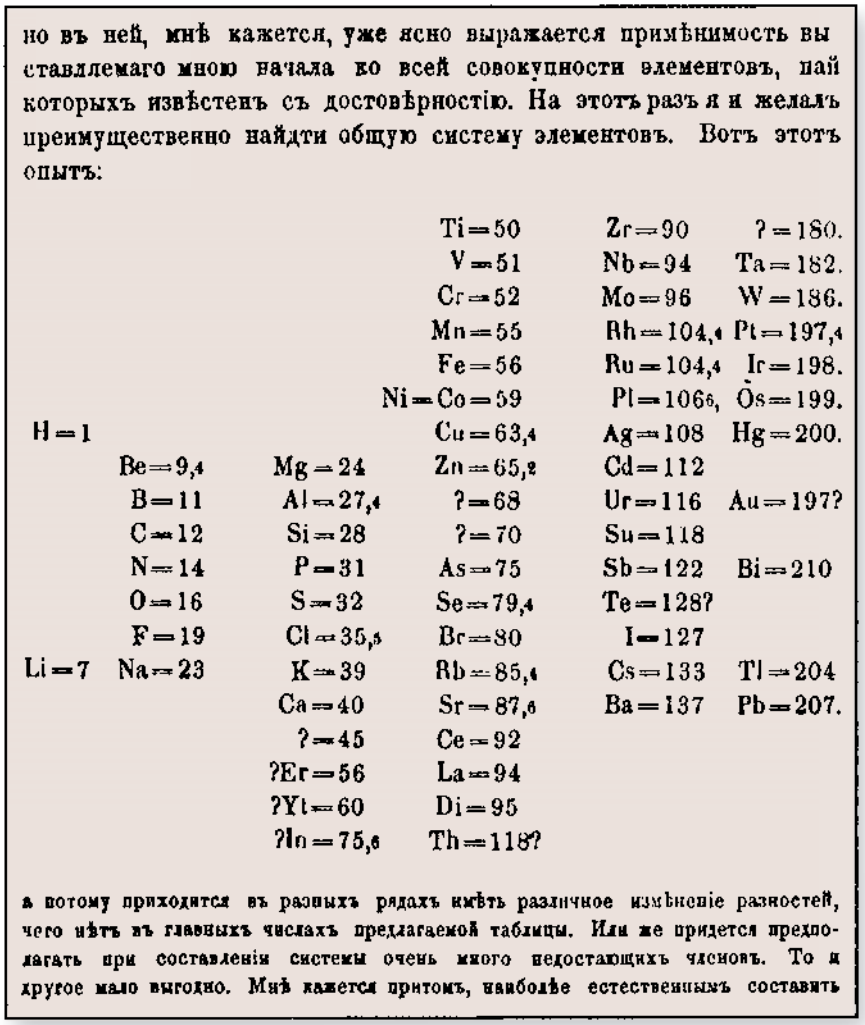
FIGURE 5-2 In his first published periodic table, Mendeleev arranged the elements in vertical periods according to relative atomic mass. The atomic mass for each element is indicated by the number following the element's symbol. The unknown elements indicated by question marks at estimated atomic masses 45, 68, and 70 were later identified as scandium, Sc, gallium, Ga, and germanium, Ge.



но въ ней, мнѣ кажется, уже ясно выражается примѣнимость вы ставляемаго мною начала ко всей совокупности элементовъ, пай которыхъ извѣстенъ съ достовѣрностію. На этотъ разъ я и желалъ преимущественно найдти общую систему элементовъ. Вотъ этотъ опытъ:

			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

а потому приходится въ разныхъ рядахъ имѣть различное измѣненіе разностей, чего нѣтъ въ главныхъ числахъ предлагаемой таблицы. Или же придется предполагать при составленіи системы очень много недостающихъ членовъ. То и другое мало выгодно. Мнѣ кажется притомъ, наиболѣе естественнымъ составить

Mendeleev created a table in which elements with similar properties were grouped together—a periodic table of the elements. His first periodic table, shown in Figure 5-2, was published in 1869. Note that Mendeleev placed iodine, I (atomic mass 127), after tellurium, Te (atomic mass 128). Although this contradicted the pattern of listing the elements in order of increasing atomic mass, it allowed Mendeleev to place tellurium in a group of elements with which it shares similar properties. Reading horizontally across Mendeleev's table, this group includes oxygen, O, sulfur, S, and selenium, Se. Iodine could also, then, be placed in the group it resembles chemically, which includes fluorine, F, chlorine, Cl, and bromine, Br.

Mendeleev's procedure left several empty spaces in his periodic table (see Figure 5-2). In 1871, the Russian chemist boldly predicted the existence and properties of the elements that would fill three of the spaces. By 1886, all three elements had been discovered. Today these elements are known as scandium, Sc, gallium, Ga, and germanium, Ge. Their properties are strikingly similar to those predicted by Mendeleev.

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The success of Mendeleev's predictions persuaded most chemists to accept his periodic table and earned him credit as the discoverer of the periodic law. Two questions remained, however. (1) Why could most of the elements be arranged in the order of increasing atomic mass but a few could not? (2) What was the reason for chemical periodicity?

Moseley and the Periodic Law

The first question was not answered until more than 40 years after Mendeleev's first periodic table was published. In 1911, the English scientist Henry Moseley, who was working with Ernest Rutherford, examined the spectra of 38 different metals. When analyzing his data, Moseley discovered a previously unrecognized pattern. The elements in the periodic table fit into patterns better when they were arranged in increasing order according to nuclear charge, or the number of protons in the nucleus. Moseley's work led to both the modern definition of atomic number and the recognition that atomic number, not atomic mass, is the basis for the organization of the periodic table.

Moseley's discovery was consistent with Mendeleev's ordering of the periodic table by properties rather than strictly by atomic mass. For example, according to Moseley, tellurium, with an atomic number of 52, belongs before iodine, which has an atomic number of 53. Today, Mendeleev's principle of chemical periodicity is correctly stated in what is known as the **periodic law:** *The physical and chemical properties of the elements are periodic functions of their atomic numbers.* In other words, when the elements are arranged in order of increasing atomic number, elements with similar properties appear at regular intervals.

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The Modern Periodic Table

The periodic table has undergone extensive change since Mendeleev's time (see Figure 5-6 on pages 130–131). Chemists have discovered new elements and, in more recent years, synthesized new ones in the laboratory. Each of the more than 40 new elements, however, can be placed in a group of other elements with similar properties. *The* **periodic table** *is an arrangement of the elements in order of their atomic numbers so that elements with similar properties fall in the same column, or group.*

The Noble Gases

Perhaps the most significant addition to the periodic table came with the discovery of the noble gases. In 1894, English physicist John William Strutt (Lord Rayleigh) and Scottish chemist Sir William Ramsay discovered argon, Ar, a gas in the atmosphere that had previously escaped notice because of its total lack of chemical reactivity. Back in 1868,

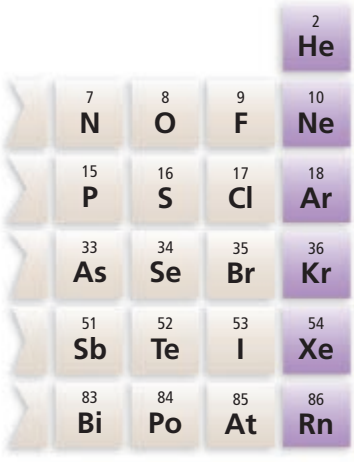

FIGURE 5-3 The noble gases, also known as the Group 18 elements, are all rather unreactive. As you will read, the reason for this low reactivity also accounts for the special place occupied by the noble gases in the periodic table.

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another noble gas, helium, He, had been discovered as a component of the sun, based on the emission spectrum of sunlight. In 1895, Ramsay showed that helium also exists on Earth.

In order to fit argon and helium into the periodic table, Ramsay proposed a new group. He placed this group between the groups now known as Group 17 (the fluorine family) and Group 1 (the lithium family). In 1898, Ramsay discovered two more noble gases to place in his new group, krypton, Kr, and xenon, Xe. The final noble gas, radon, Rn, was discovered in 1900 by the German scientist Friedrich Ernst Dorn.

The Lanthanides

The next step in the development of the periodic table was completed in the early 1900s. It was then that the puzzling chemistry of the lanthanides was finally understood. *The* **lanthanides** *are the 14 elements with atomic numbers from 58 (cerium, Ce) to 71 (lutetium, Lu).* Because these elements are so similar in chemical and physical properties, the process of separating and identifying them was a tedious task that required the effort of many chemists.

The Actinides

Another major step in the development of the periodic table was the discovery of the actinides. *The* **actinides** *are the 14 elements with atomic numbers from 90 (thorium, Th) to 103 (lawrencium, Lr).* The lanthanides and actinides belong in Periods 6 and 7, respectively, of the periodic table, between the elements of Groups 3 and 4. To save space, the lanthanides and actinides are usually set off below the main portion of the periodic table, as shown in Figure 5-6 on pages 130–131.

Periodicity

Periodicity with respect to atomic number can be observed in any group of elements in the periodic table. Consider the noble gases of Group 18. The first noble gas is helium, He. It has an atomic number of 2. The elements following helium in atomic number have completely different properties until the next noble gas, neon, Ne, which has an atomic number of 10, is reached. The remaining noble gases in order of increasing atomic number are argon (Ar, atomic number 18), krypton (Kr, atomic number 36), xenon (Xe, atomic number 54), and radon (Rn, atomic number 86). The differences in atomic number between successive noble gases are shown in Figure 5-4. Also shown in Figure 5-4 are atomic-number differences between the elements of Group 1, which are all solid, silvery metals. As you can see, the differences in atomic number between the Group 1 metals follow the same pattern as the differences in atomic number between the noble gases.

Starting with the first member of Groups 13–17, a similar periodic pattern is repeated. The atomic number of each successive element is 8, 18, 18, and 32 higher than the atomic number of the element above it. In Section 5-2, you will see that the second mystery presented by Mendeleev's periodic table—the reason for periodicity—is explained by the arrangement of the electrons around the nucleus.

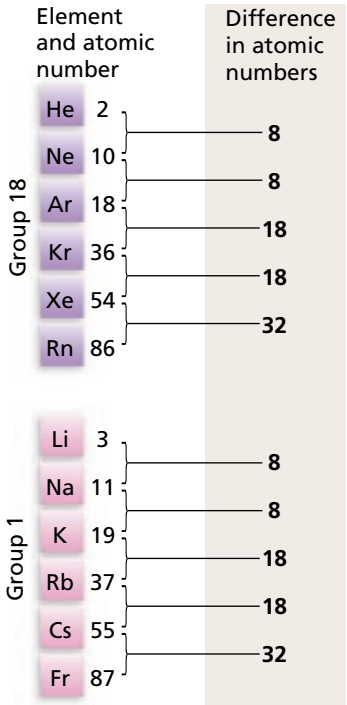

FIGURE 5-4 In each of Groups 1 and 18, the differences between the atomic numbers of successive elements are 8, 8, 18, 18, and 32, respectively. Groups 2 and 13–17 follow a similar pattern.

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Quick LAB

Designing Your Own Periodic Table

Materials

- index cards

Question

Can you design your own periodic table using information similar to that available to Mendeleev?

Procedure

1. Write down the information available for each element on separate index cards. The following information is appropriate: a letter of the alphabet (A, B, C, etc.) to identify each element; atomic mass; state; density; melting point; boiling point; and any other readily observable physical properties. Do not write the name of the element on the index card, but keep a separate list indicating the letters you have assigned to each element.
2. Organize the cards for the elements in a logical pattern as you think Mendeleev might have done.

Discussion

1. Keeping in mind that the information you have is similar to that available to Mendeleev in 1869, answer the following questions.
   - **a.** Why are atomic masses given instead of atomic numbers?
   - **b.** Can you identify each element by name?
2. How many groups of elements, or families, are in your periodic table? How many periods, or series, are in the table?
3. Predict the characteristics of any missing elements.When you have finished, check your work using your separate list of elements and a periodic table.

SECTION REVIEW

1. a. Who is credited with developing a method that led to the determination of standard relative atomic masses?
   b. Who discovered the periodic law?
   c. Who established atomic numbers as the basis for organizing the periodic table?
2. State the periodic law.
3. Name three sets of elements added to the periodic table after Mendeleev's time.
4. How do the atomic numbers of the elements within each of Groups 1, 2, and 13–18 of the periodic table vary? (Refer to Figure 5-4 as a guide.)

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SECTION 5-2

OBJECTIVES

- Describe the relationship between electrons in sublevels and the length of each period of the periodic table.
- Locate and name the four blocks of the periodic table. Explain the reasons for these names.
- Discuss the relationship between group configurations and group numbers.
- Describe the locations in the periodic table and the general properties of the alkali metals, the alkaline-earth metals, the halogens, and the noble gases.

Electron Configuration and the Periodic Table

The Group 18 elements of the periodic table (the noble gases) undergo few chemical reactions. This stability results from the gases' special electron configurations. Helium's highest occupied level, the 1*s* orbital, is completely filled with electrons. And the highest occupied levels of the other noble gases contain stable octets. Generally the electron configuration of an atom's highest occupied energy level governs the atom's chemical properties.

Periods and Blocks of the Periodic Table

While the elements are arranged vertically in the periodic table in groups that share similar chemical properties, they are also organized horizontally in rows, or *periods*. (As shown in Figure 5-6, there are a total of seven periods of elements in the modern periodic table.) As can be seen in Table 5-1, the length of each period is determined by the number of electrons that can occupy the sublevels being filled in that period.

TABLE 5-1 *Relationship Between Period Length and Sublevels Being Filled in the Periodic Table*

Period number	Number of elements in period	Sublevels in order of filling
1	2	1*s*
2	8	2*s* 2*p*
3	8	3*s* 3*p*
4	18	4*s* 3*d* 4*p*
5	18	5*s* 4*d* 5*p*
6	32	6*s* 4*f* 5*d* 6*p*
7	32	7*s* 5*f* 6*d*, etc.

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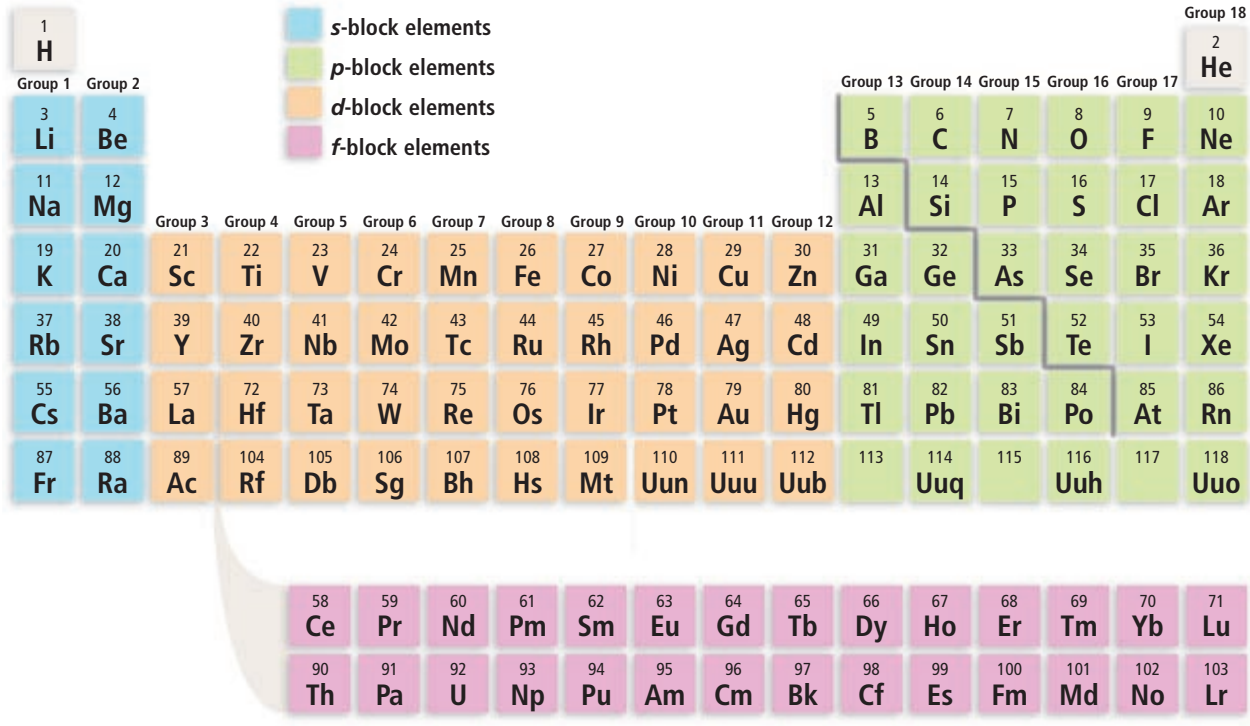
In the first period, the 1*s* sublevel is being filled. The 1*s* sublevel can hold a total of two electrons. Therefore, the first period consists of two elements—hydrogen and helium. In the second period, the 2*s* sublevel, which can hold two electrons, and the 2*p* sublevel, which can hold six electrons, are being filled. Consequently, the second period totals eight elements. Similarly, filling of the 3*s* and 3*p* sublevels accounts for the eight elements of the third period. Filling 3*d* and 4*d* sublevels in addition to the *s* and *p* sublevels adds 10 elements to both the fourth and fifth periods. Therefore, each of these periods totals 18 elements. Filling 4*f* sublevels in addition to *s, p,* and *d* sublevels adds 14 elements to the sixth period, which totals 32 elements. And as new elements are created, the 29 known elements in Period 7 could, in theory, be extended to 32.

The period of an element can be determined from the element's electron configuration. For example, arsenic, As, has the electron configuration $[Ar]3d^{10}4s^24p^3$. The 4 in $4p^3$ indicates that arsenic's highest occupied energy level is the fourth energy level. Arsenic is therefore in the fourth period in the periodic table. The period and electron configuration for each element can be found in the periodic table on pages 130–131.

Based on the electron configurations of the elements, the periodic table can be divided into four blocks, the *s, p, d,* and *f* blocks. This division is illustrated in Figure 5-5. The name of each block is determined by whether an *s, p, d,* or *f* sublevel is being filled in successive elements of that block.

FIGURE 5-5 Based on the electron configurations of the elements, the periodic table can be subdivided into four sublevel blocks.

Sublevel Blocks of the Periodic Table



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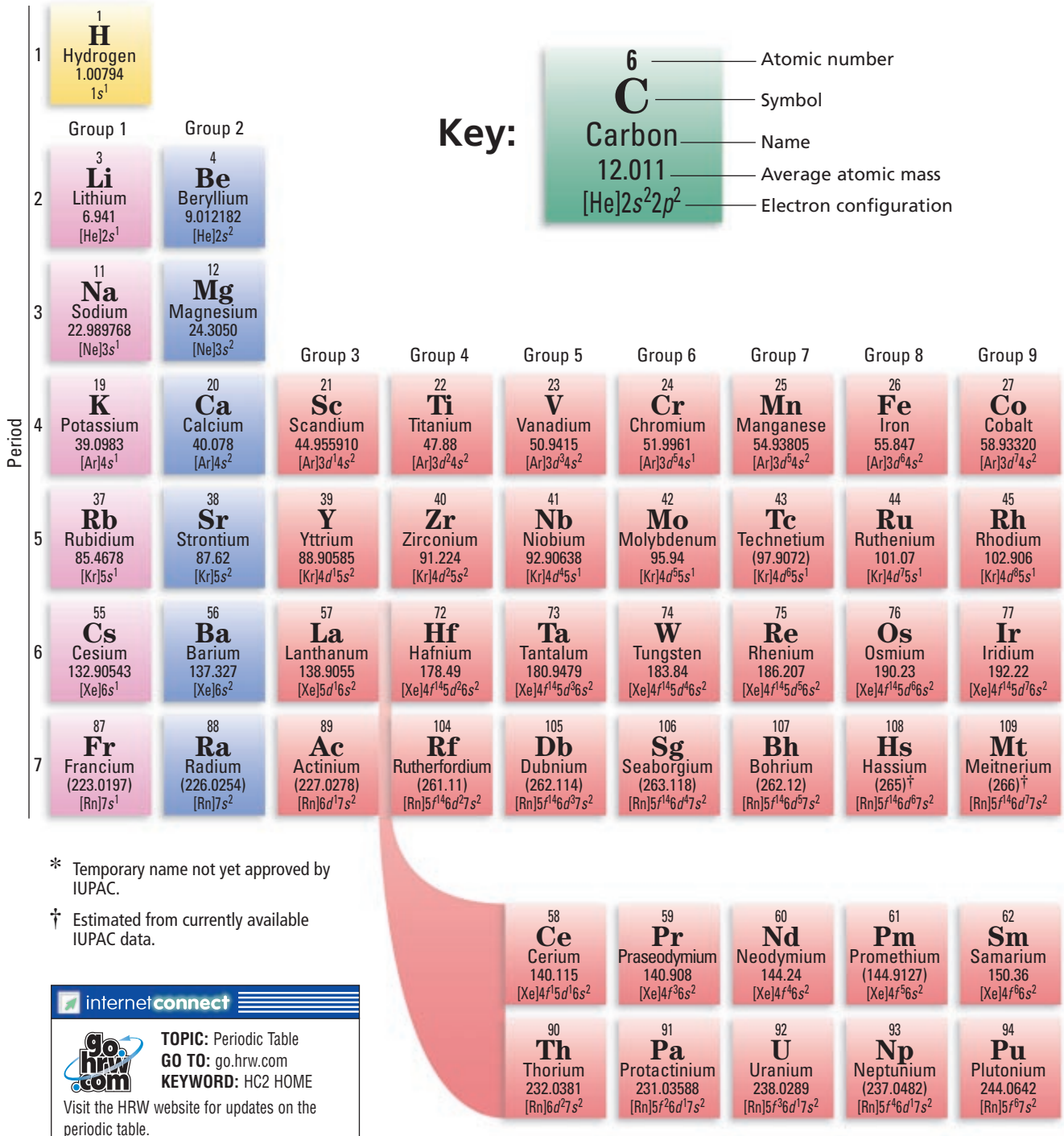
Periodic Table of the Elements


Key:
6
C
Carbon
12.011
[He]2s²2p²
Atomic number
Symbol
Name
Average atomic mass
Electron configuration
Period
Group 1
Group 2
Group 3
Group 4
Group 5
Group 6
Group 7
Group 8
Group 9
1 H Hydrogen 1.00794 1s¹
2 Li Lithium 6.941 [He]2s¹
2 Be Beryllium 9.012182 [He]2s²
3 Na Sodium 22.989768 [Ne]3s¹
3 Mg Magnesium 24.3050 [Ne]3s²
4 K Potassium 39.0983 [Ar]4s¹
4 Ca Calcium 40.078 [Ar]4s²
4 Sc Scandium 44.955910 [Ar]3d¹4s²
4 Ti Titanium 47.88 [Ar]3d²4s²
4 V Vanadium 50.9415 [Ar]3d³4s²
4 Cr Chromium 51.9961 [Ar]3d⁵4s¹
4 Mn Manganese 54.93805 [Ar]3d⁵4s²
4 Fe Iron 55.847 [Ar]3d⁶4s²
4 Co Cobalt 58.93320 [Ar]3d⁷4s²
5 Rb Rubidium 85.4678 [Kr]5s¹
5 Sr Strontium 87.62 [Kr]5s²
5 Y Yttrium 88.90585 [Kr]4d¹5s²
5 Zr Zirconium 91.224 [Kr]4d²5s²
5 Nb Niobium 92.90638 [Kr]4d⁴5s¹
5 Mo Molybdenum 95.94 [Kr]4d⁵5s¹
5 Tc Technetium (97.9072) [Kr]4d⁶5s¹
5 Ru Ruthenium 101.07 [Kr]4d⁷5s¹
5 Rh Rhodium 102.906 [Kr]4d⁸5s¹
6 Cs Cesium 132.90543 [Xe]6s¹
6 Ba Barium 137.327 [Xe]6s²
6 La Lanthanum 138.9055 [Xe]5d¹6s²
6 Hf Hafnium 178.49 [Xe]4f¹⁴5d²6s²
6 Ta Tantalum 180.9479 [Xe]4f¹⁴5d³6s²
6 W Tungsten 183.84 [Xe]4f¹⁴5d⁴6s²
6 Re Rhenium 186.207 [Xe]4f¹⁴5d⁵6s²
6 Os Osmium 190.23 [Xe]4f¹⁴5d⁶6s²
6 Ir Iridium 192.22 [Xe]4f¹⁴5d⁷6s²
7 Fr Francium (223.0197) [Rn]7s¹
7 Ra Radium (226.0254) [Rn]7s²
7 Ac Actinium (227.0278) [Rn]6d¹7s²
7 Rf Rutherfordium (261.11) [Rn]5f¹⁴6d²7s²
7 Db Dubnium (262.114) [Rn]5f¹⁴6d³7s²
7 Sg Seaborgium (263.118) [Rn]5f¹⁴6d⁴7s²
7 Bh Bohrium (262.12) [Rn]5f¹⁴6d⁵7s²
7 Hs Hassium (265)† [Rn]5f¹⁴6d⁶7s²
7 Mt Meitnerium (266)† [Rn]5f¹⁴6d⁷7s²
58 Ce Cerium 140.115 [Xe]4f¹5d¹6s²
59 Pr Praseodymium 140.908 [Xe]4f³6s²
60 Nd Neodymium 144.24 [Xe]4f⁴6s²
61 Pm Promethium (144.9127) [Xe]4f⁵6s²
62 Sm Samarium 150.36 [Xe]4f⁶6s²
90 Th Thorium 232.0381 [Rn]6d²7s²
91 Pa Protactinium 231.03588 [Rn]5f²6d¹7s²
92 U Uranium 238.0289 [Rn]5f³6d¹7s²
93 Np Neptunium (237.0482) [Rn]5f⁴6d¹7s²
94 Pu Plutonium 244.0642 [Rn]5f⁶7s²

* Temporary name not yet approved by IUPAC.

† Estimated from currently available IUPAC data.

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FIGURE 5-6 In the common periodic table, the elements are arranged in vertical groups and in horizontal periods.

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Metals
- Alkali metals
- Alkaline earth metals
- Transition metals
- Other metals

Metalloids
- Semiconductors

Nonmetals
- Halogens
- Other nonmetals
- Noble gases

Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18	Period
								2 **He** Helium 4.002602 $1s^2$	1
			5 **B** Boron 10.811 $[He]2s^22p^1$	6 **C** Carbon 12.011 $[He]2s^22p^2$	7 **N** Nitrogen 14.00674 $[He]2s^22p^3$	8 **O** Oxygen 15.9994 $[He]2s^22p^4$	9 **F** Fluorine 18.9984032 $[He]2s^22p^5$	10 **Ne** Neon 20.1797 $[He]2s^22p^6$	2
			13 **Al** Aluminum 26.981539 $[Ne]3s^23p^1$	14 **Si** Silicon 28.0855 $[Ne]3s^23p^2$	15 **P** Phosphorus 30.9738 $[Ne]3s^23p^3$	16 **S** Sulfur 32.066 $[Ne]3s^23p^4$	17 **Cl** Chlorine 35.4527 $[Ne]3s^23p^5$	18 **Ar** Argon 39.948 $[Ne]3s^23p^6$	3
28 **Ni** Nickel 58.6934 $[Ar]3d^84s^2$	29 **Cu** Copper 63.546 $[Ar]3d^{10}4s^1$	30 **Zn** Zinc 65.39 $[Ar]3d^{10}4s^2$	31 **Ga** Gallium 69.723 $[Ar]3d^{10}4s^24p^1$	32 **Ge** Germanium 72.61 $[Ar]3d^{10}4s^24p^2$	33 **As** Arsenic 74.92159 $[Ar]3d^{10}4s^24p^3$	34 **Se** Selenium 78.96 $[Ar]3d^{10}4s^24p^4$	35 **Br** Bromine 79.904 $[Ar]3d^{10}4s^24p^5$	36 **Kr** Krypton 83.80 $[Ar]3d^{10}4s^24p^6$	4
46 **Pd** Palladium 106.42 $[Kr]4d^{10}5s^0$	47 **Ag** Silver 107.8682 $[Kr]4d^{10}5s^1$	48 **Cd** Cadmium 112.411 $[Kr]4d^{10}5s^2$	49 **In** Indium 114.818 $[Kr]4d^{10}5s^25p^1$	50 **Sn** Tin 118.710 $[Kr]4d^{10}5s^25p^2$	51 **Sb** Antimony 121.757 $[Kr]4d^{10}5s^25p^3$	52 **Te** Tellurium 127.60 $[Kr]4d^{10}5s^25p^4$	53 **I** Iodine 126.904 $[Kr]4d^{10}5s^25p^5$	54 **Xe** Xenon 131.29 $[Kr]4d^{10}5s^25p^6$	5
78 **Pt** Platinum 195.08 $[Xe]4f^{14}5d^96s^1$	79 **Au** Gold 196.96654 $[Xe]4f^{14}5d^{10}6s^1$	80 **Hg** Mercury 200.59 $[Xe]4f^{14}5d^{10}6s^2$	81 **Tl** Thallium 204.3833 $[Xe]4f^{14}5d^{10}6s^26p^1$	82 **Pb** Lead 207.2 $[Xe]4f^{14}5d^{10}6s^26p^2$	83 **Bi** Bismuth 208.98037 $[Xe]4f^{14}5d^{10}6s^26p^3$	84 **Po** Polonium (208.9824) $[Xe]4f^{14}5d^{10}6s^26p^4$	85 **At** Astatine (209.9871) $[Xe]4f^{14}5d^{10}6s^26p^5$	86 **Rn** Radon (222.0176) $[Xe]4f^{14}5d^{10}6s^26p^6$	6
110 **Uun*** Ununnilium (269)† $[Rn]5f^{14}6d^97s^1$	111 **Uuu*** Unununium (272)† $[Rn]5f^{14}6d^{10}7s^1$	112 **Uub*** Unubium (277)† $[Rn]5f^{14}6d^{10}7s^2$	113	114 **Uuq*** Ununquadium (285)† $[Rn]5f^{14}6d^{10}7s^27p^2$	115	116 **Uuh*** Ununhexium (289)† $[Rn]5f^{14}6d^{10}7s^27p^4$	117	118 **Uuo*** Ununoctium (293)† $[Rn]5f^{14}6d^{10}7s^27p^6$	7

63 **Eu** Europium 151.966 $[Xe]4f^76s^2$	64 **Gd** Gadolinium 157.25 $[Xe]4f^75d^16s^2$	65 **Tb** Terbium 158.92534 $[Xe]4f^96s^2$	66 **Dy** Dysprosium 162.50 $[Xe]4f^{10}6s^2$	67 **Ho** Holmium 164.930 $[Xe]4f^{11}6s^2$	68 **Er** Erbium 167.26 $[Xe]4f^{12}6s^2$	69 **Tm** Thulium 168.93421 $[Xe]4f^{13}6s^2$	70 **Yb** Ytterbium 173.04 $[Xe]4f^{14}6s^2$	71 **Lu** Lutetium 174.967 $[Xe]4f^{14}5d^16s^2$
95 **Am** Americium (243.0614) $[Rn]5f^77s^2$	96 **Cm** Curium (247.0703) $[Rn]5f^76d^17s^2$	97 **Bk** Berkelium (247.0703) $[Rn]5f^97s^2$	98 **Cf** Californium (251.0796) $[Rn]5f^{10}7s^2$	99 **Es** Einsteinium (252.083) $[Rn]5f^{11}7s^2$	100 **Fm** Fermium (257.0951) $[Rn]5f^{12}7s^2$	101 **Md** Mendelevium (258.10) $[Rn]5f^{13}7s^2$	102 **No** Nobelium (259.1009) $[Rn]5f^{14}7s^2$	103 **Lr** Lawrencium (262.11) $[Rn]5f^{14}6d^17s^2$

The atomic masses listed in this table reflect the precision of current measurements. (Values listed in parentheses are those of the element's most stable or most common isotope.) In calculations throughout the text, however, atomic masses have been rounded to two places to the right of the decimal.

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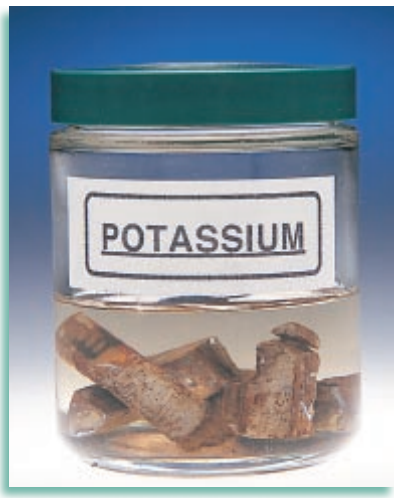
(a)



(b)

FIGURE 5-7 (a) Like other alkali metals, potassium reacts so strongly with water that (b) it must be stored in kerosene or oil to prevent it from reacting with moisture in the air.

The *s*-Block Elements: Groups 1 and 2

The elements of the *s* block are chemically reactive *metals*. The Group 1 metals are more reactive than those of Group 2. The outermost energy level in an atom of each Group 1 element contains a single *s* electron. For example, the configurations of lithium and sodium are $[He]2s^1$ and $[Ne]3s^1$, respectively. As you will learn in Section 5-3, the ease with which the single electron is lost helps to make the Group 1 metals extremely reactive. Using n for the number of the highest occupied energy level, the outer, or group, configurations of the Group 1 and 2 elements are written ns^1 and ns^2, respectively. For example, the configuration of Na is $[Ne]3s^1$, so the group configuration is written ns^1, where $n = 3$.

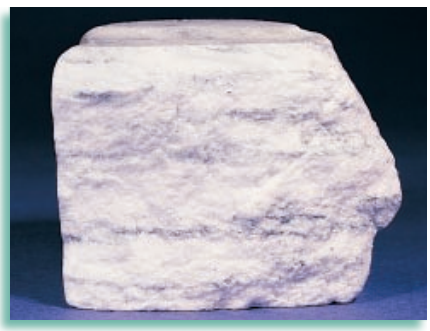
The elements of Group 1 of the periodic table (lithium, sodium, potassium, rubidium, cesium, and francium) are known as the **alkali metals.** In their pure state, all of the alkali metals have a silvery appearance and are soft enough to cut with a knife. However, because they are so reactive, alkali metals are not found in nature as free elements. They combine vigorously with most nonmetals. And they react strongly with water to produce hydrogen gas and aqueous solutions of substances known as alkalis. Because of their extreme reactivity with air or moisture, alkali metals are usually stored in kerosene. Proceeding down the column, the elements of Group 1 melt at successively lower temperatures.

The elements of Group 2 of the periodic table (beryllium, magnesium, calcium, strontium, barium, and radium) are called the **alkaline-earth metals.** Atoms of alkaline-earth metals contain a pair of electrons in their outermost *s* sublevel. Consequently, the group configuration for Group 2 is ns^2. The Group 2 metals are harder, denser, and stronger than the alkali metals. They also have higher melting points. Although they are less reactive than the alkali metals, the alkaline-earth metals are also too reactive to be found in nature as free elements.

Hydrogen and Helium

Before discussing the other blocks of the periodic table, let's consider two special cases in the classification of the elements—hydrogen and helium. Hydrogen has an electron configuration of $1s^1$, but despite the ns^1 configuration, it does not share the same properties as the elements

(a)



(b)

FIGURE 5-8 Calcium, an alkaline-earth metal, is too reactive to be found in nature in its pure state (a). Instead, it exists in compounds, such as in the minerals that make up marble (b).

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of Group 1. Although it is located above the Group 1 elements in many periodic tables, hydrogen is a unique element, with properties that do not closely resemble those of any group.

Like the Group 2 elements, helium has an ns^2 group configuration. Yet it is part of Group 18. Because its highest occupied energy level is filled by two electrons, helium possesses special chemical stability, exhibiting the unreactive nature of a Group 18 element. By contrast, the Group 2 metals have no special stability; their highest occupied energy levels are not filled because each metal has an empty available *p* sublevel.

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SAMPLE PROBLEM 5-1

a. Without looking at the periodic table, give the group, period, and block in which the element with the electron configuration [Xe]$6s^2$ is located.

b. Without looking at the periodic table, write the electron configuration for the Group 1 element in the third period. Is this element likely to be more active or less active than the element described in (a)?

SOLUTION

a. The element is in Group 2, as indicated by the group configuration of ns^2. It is in the sixth period, as indicated by the highest principal quantum number in its configuration, 6. The element is in the *s* block.

b. In a third-period element, the highest occupied energy level is the third main energy level, $n = 3$. The 1*s*, 2*s*, and 2*p* sublevels are completely filled (see Table 5-1). A Group 1 element has a group configuration of ns^1, which indicates a single electron in its highest *s* sublevel. Therefore, this element has the following configuration.

$$1s^2 2s^2 2p^6 3s^1 \quad \text{or} \quad [\text{Ne}]3s^1$$

Because it is in Group 1 (the alkali metals), this element is likely to be more reactive than the element described in (a), which is in Group 2 (the alkaline-earth metals).

PRACTICE

1. Without looking at the periodic table, give the group, period, and block in which the element with the electron configuration [Kr]$5s^1$ is located.
2. a. Without looking at the periodic table, write the group configuration for the Group 2 elements.
   b. Without looking at the periodic table, write the complete electron configuration for the Group 2 element in the fourth period.
   c. Refer to Figure 5-6 to identify the element described in (b). Then write the element's noble-gas notation.
   d. How does the reactivity of the element in (b) compare with the reactivity of the element in Group 1 of the same period?

Answer

1. Group 1, fifth period, *s* block
2. a. ns^2
   b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
   c. Ca, [Ar]$4s^2$
   d. The element is in Group 2, so it is probably less reactive than the Group 1 element of the same period.

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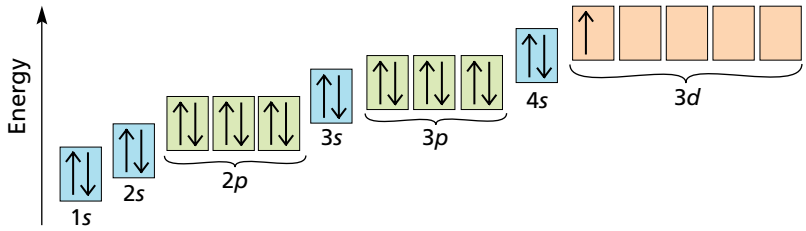


FIGURE 5-9 The diagram shows the electron configuration of scandium, Sc, the Group 3 element of the fourth period. In general, the $(n-1)d$ sublevel in Groups 3–12 is occupied by electrons after the ns sublevel is filled.

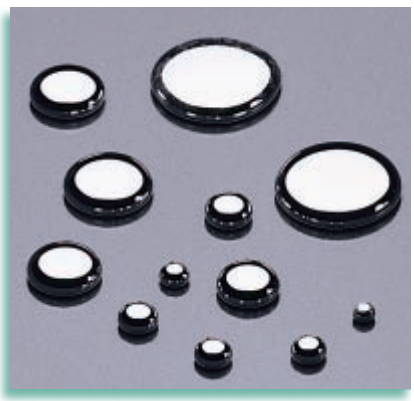
The *d*-Block Elements: Groups 3–12

For energy level n, there are n possible sublevels, so the d sublevel first appears when $n = 3$. This $3d$ sublevel is slightly higher in energy than the $4s$ sublevel, so these are filled in the order $4s3d$ (see Figure 5-9). This order of filling is also seen for higher values of n. Each d sublevel consists of five orbitals with a maximum of two electrons each, or up to 10 electrons possible in each d sublevel. In addition to the two ns electrons of Group 2, atoms of the Group 3 elements each have one electron in the d sublevel of the $(n-1)$ energy level. The group configuration for Group 3 is therefore $(n-1)d^1ns^2$. Atoms of the Group 12 elements have 10 electrons in the d sublevel plus two electrons in the ns sublevel. The group configuration for Group 12 is $(n-1)d^{10}ns^2$.

As you read in Chapter 4, some deviations from orderly d sublevel filling occur in Groups 4–11. As a result, elements in these d-block groups, unlike those in s-block and p-block groups, do not necessarily have identical outer electron configurations. For example, in Group 10, nickel, Ni, has the electron configuration $[Ar]3d^84s^2$. Palladium, Pd, has the configuration $[Kr]4d^{10}5s^0$. And platinum, Pt, has the configuration $[Xe]4f^{14}5d^96s^1$. Notice, however, that in each case the sum of the outer s and d electrons is equal to the group number.

The d-block elements are metals with typical metallic properties and are often referred to as **transition elements.** They are good conductors of electricity and have a high luster. They are typically less reactive than the alkali metals and the alkaline-earth metals. Some are so unreactive that they do not easily form compounds, existing in nature as free elements. Palladium, platinum, and gold are among the least reactive of all the elements. Some d-block elements are shown in Figure 5-10.

FIGURE 5-10 Mercury, tungsten, and vanadium are transition elements. Locate them in the d block of the periodic table on page 129.


Mercury

Tungsten

Vanadium

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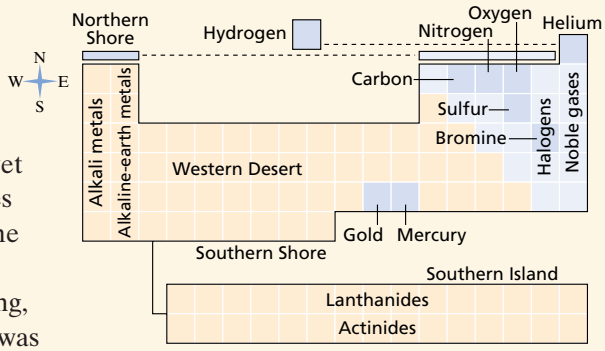
The Wild Kingdom

From *The Periodic Kingdom: A Journey Into the World of the Chemical Elements* by P. W. Atkins

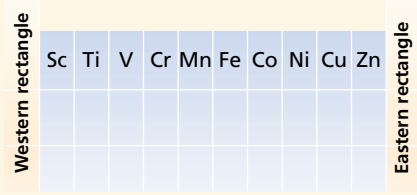


The general layout of the Periodic Kingdom.

Welcome to the Periodic Kingdom. This is a land of the imagination, but it is closer to reality than it appears to be. This is the kingdom of the chemical elements, the substances from which everything tangible is made. It is not an extensive country, for it consists of only a hundred or so regions . . . yet it accounts for everything material in our actual world. From the hundred elements that are at the center of our story, all planets, rocks, vegetation, and animals are made. These elements are the basis of the air, the oceans, and the Earth itself. We stand on the elements, we eat the elements, we *are* the elements. Because our brains are made up of elements, even our opinions are, in a sense, properties of the elements and hence inhabitants of the kingdom.

Even from . . . far above the country, we can see broad features of the landscape. There are the glittering, lustrous regions made up of metals and lying together in what we shall call the Western Desert. This desert is broadly uniform, but there is a subtlety of shades, indicating a variety of characteristics. Here and there are gentle splashes of color, such as the familiar glint of gold and the blush of copper. How remarkable it is that these desert lands make up so much of the kingdom . . . yet the kingdom supplies such luxuriance in the real world!

Generally speaking, the Western Desert was explored and exploited from east to west; that is, technology and industry made use of them in that order. Copper displaced stone to give us the Bronze Age. Then, as the explorers pressed westward, applying ever more vigorous means of discovery, they encountered iron and used it to fabricate more effective weaponry . . . The strongest states enjoyed freedom from constant aggression, and this gave them time for scholarship; thus in due course explorers were able to penetrate into more distant western regions of the desert.



The Isthmus

Deep in the Western Desert, in an isthmuslike zone running from zinc on the east to scandium on the west, they finally stumbled upon titanium, a remarkable prize indeed. Titanium has exactly the properties that a society bent on high technology needs if it is to take to the skies: this is a metal that is tough and resistant to corrosion, yet light, and it is typical of its part of the Western Desert. Titanium and its neighbors vanadium and molybdenum, in alliance with iron, form the durable steels that enable us to chop through stone and build on a massive scale. It is a remarkable feature of the Periodic Kingdom that the Isthmus . . . has provided so many of the workhorses of our society, and that its members so readily form alliances with one another.

Reading for Meaning

What does Atkins mean when he says that metals of the Isthmus form "alliances" with one another? What does this imply about these elements?

Read Further

Atkins remarks that titanium has properties that are well-suited for a high-tech society. Find out how we obtain titanium, and list five ways that it is used in our society.

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SAMPLE PROBLEM 5-2

An element has the electron configuration [Kr]$4d^5 5s^1$. Without looking at the periodic table, identify the period, block, and group in which this element is located. Then consult the periodic table to identify this element and the others in its group.

SOLUTION

The number of the highest occupied energy level is five, so the element is in the fifth period. There are five electrons in the *d* sublevel. This means that the *d* sublevel is incompletely filled because it can hold 10 electrons. Therefore, the element is in the *d* block. For *d*-block elements, the number of electrons in the *ns* sublevel (1) plus the number of electrons in the $(n - 1)d$ sublevel (5) equals the group number, 6. This is the Group 6 element in the fifth period. The element is molybdenum. The others in Group 6 are chromium, tungsten, and seaborgium.

PRACTICE

1. Without looking at the periodic table, identify the period, block, and group in which the element with the electron configuration [Ar]$3d^8 4s^2$ is located.

   Answer
   1. fourth period, *d* block, Group 10

2. a. Without looking at the periodic table, write the outer electron configuration for the Group 12 element in the fifth period.

   2. a. $4d^{10}5s^2$

   b. Refer to the periodic table to identify the element described in (a) and to write the element's noble-gas notation.

   b. Cd, [Kr]$4d^{10}5s^2$

The *p*-Block Elements: Groups 13–18

The *p*-block elements consist of all the elements of Groups 13–18 except helium. Electrons add to a *p* sublevel only after the *s* sublevel in the same energy level is filled. Therefore, atoms of all *p*-block elements contain two electrons in the *ns* sublevel. *The p-block elements together with the s-block elements are called the* **main-group elements.** For Group 13 elements, the added electron enters the *np* sublevel, giving a group configuration of ns^2np^1. Atoms of Group 14 elements contain two electrons in the *p* sublevel, giving ns^2np^2 for the group configuration. This pattern continues in Groups 15–18. In Group 18, the stable noble-gas configuration of ns^2np^6 is reached. The relationships among group numbers and electron configurations for all the groups are summarized in Table 5-2.

For atoms of *p*-block elements, the total number of electrons in the highest occupied level is equal to the group number minus 10. For example, bromine is in Group 17. It has 17 – 10 = 7 electrons in its highest energy level. Because atoms of *p*-block elements contain two electrons in the *ns* sublevel, we know that bromine has five electrons in its outer *p* sublevel. The electron configuration of bromine is [Ar]$3d^{10}4s^2 4p^5$.

The properties of elements of the *p* block vary greatly. At its right-hand end, the *p* block includes all of the *nonmetal*s except hydrogen and helium. All six of the *metalloids* (boron, silicon, germanium, arsenic,

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TABLE 5-2 Relationships Among Group Numbers, Blocks, and Electron Configurations

Group number	Group configuration	Block	Comments
1, 2	$ns^{1,2}$	*s*	One or two electrons in *ns* sublevel
3–12	$(n-1)d^{1-10}ns^{0-2}$	*d*	Sum of electrons in *ns* and $(n-1)d$ levels equals group number
13–18	ns^2np^{1-6}	*p*	Number of electrons in *np* sublevel equals group number minus 12

antimony, and tellurium) are also in the *p* block. At the left-hand side and bottom of the block, there are eight *p*-block metals. The locations of the nonmetals, metalloids, and metals in the *p* block are shown with distinctive colors in Figure 5-6 and in the periodic table printed on the inside back cover of this textbook.

The elements of Group 17 (fluorine, chlorine, bromine, iodine, and astatine) are known as the **halogens.** The halogens are the most reactive nonmetals. They react vigorously with most metals to form examples of the type of compound known as salts. As you will see later, the reactivity of the halogens is based on the presence of seven electrons in their outer energy levels—one electron short of the stable noble-gas configuration. Fluorine and chlorine are gases at room temperature, bromine is a reddish liquid, and iodine is a dark purple solid. Astatine is a synthetic element prepared in only very small quantities. Most of its properties are estimated, although it is known to be a solid.

The metalloids, or semiconducting elements, fall on both sides of a line separating nonmetals and metals in the *p* block. They are mostly brittle solids with some properties of metals and some of nonmetals. The metalloid elements have electrical conductivity intermediate between that of metals, which are good conductors, and nonmetals, which are nonconductors.

The metals of the *p* block are generally harder and denser than the *s*-block alkaline-earth metals, but softer and less dense than the *d*-block metals. With the exception of bismuth, these metals are sufficiently reactive to be found in nature only in the form of compounds. Once obtained as free metals, however, they are stable in the presence of air.

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FIGURE 5-11 Fluorine, chlorine, bromine, and iodine are members of Group 17 of the periodic table, also known as the halogens. Locate the halogens in the *p* block of the periodic table on page 129.

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SAMPLE PROBLEM 5-3

Without looking at the periodic table, write the outer electron configuration for the Group 14 element in the second period. Then name the element, and identify it as a metal, nonmetal, or metalloid.

SOLUTION

The group number is higher than 12, so the element is in the *p* block. The total number of electrons in the highest occupied *s* and *p* sublevels is therefore equal to the group number minus ten, 14 – 10 = 4. With two electrons in the *s* sublevel, two electrons must also be present in the 2*p* sublevel, giving an outer electron configuration of $2s^2 2p^2$. The element is carbon, C, which is a nonmetal.

PRACTICE

1. a. Without looking at the periodic table, write the outer electron configuration for the Group 17 element in the third period.

   b. Name the element described in (a), and identify it as a metal, nonmetal, or metalloid.

2. a. Without looking at the periodic table, identify the period, block, and group of an element with the electron configuration $[Ar]3d^{10}4s^2 4p^3$.

   b. Name the element described in (a), and identify it as a metal, nonmetal, or metalloid.

Answer

1. a. $3s^2 3p^5$

   b. chlorine, nonmetal

2. a. fourth period, *p* block, Group 15

   b. arsenic, metalloid

The *f*-Block Elements: Lanthanides and Actinides

In the periodic table, the *f*-block elements are wedged between Groups 3 and 4 in the sixth and seventh periods. Their position reflects the fact that they involve the filling of the 4*f* sublevel. With seven 4*f* orbitals to be filled with two electrons each, there are a total of 14 *f*-block elements between lanthanum, La, and hafnium, Hf, in the sixth period. The lanthanides are shiny metals similar in reactivity to the Group 2 alkaline-earth metals.

There are also 14 *f*-block elements, the actinides, between actinium, Ac, and element 104, Rf, in the seventh period. In these elements the 5*f* sublevel is being filled with 14 electrons. The actinides are all radioactive. The first four actinides (thorium, Th, through neptunium, Np) have been found naturally on Earth. The remaining actinides are known only as laboratory-made elements.

SAMPLE PROBLEM 5-4

The electron configurations of atoms of four elements are written at the top of page 139. For each element, name the block and group in the periodic table in which it is located. Then name the element by consulting the periodic table on pages 130–131. Identify each

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element as a metal, nonmetal, or metalloid. Finally, describe it as likely to be of high reactivity or of low reactivity.

a. $[Xe]4f^{14}5d^{9}6s^{1}$
b. $[Ne]3s^{2}3p^{5}$
c. $[Ne]3s^{2}3p^{6}$
d. $[Xe]4f^{6}6s^{2}$

SOLUTION

a. The 4*f* sublevel is filled with 14 electrons. The 5*d* sublevel is partially filled with nine electrons. Therefore, this is a *d*-block element. The element is the transition metal platinum, Pt, which is in Group 10 and has a low reactivity.

b. The incompletely filled *p* sublevel shows this to be a *p*-block element. With a total of seven electrons in the *ns* and *np* sublevels, this is a Group 17 element, a halogen. The element is chlorine, Cl, and is highly reactive.

c. This element has a noble-gas configuration and thus is in Group 18 in the *p* block. The element is argon, Ar, an unreactive nonmetal and a noble gas.

d. The incomplete 4*f* sublevel shows that it is an *f*-block element and a lanthanide. Group numbers are not assigned to the *f* block. The element is samarium, Sm. The lanthanides are all reactive metals.

PRACTICE

1. For each of the following, identify the block, period, group, group name (where appropriate), element name, element type (metal, nonmetal, or metalloid), and relative reactivity (high or low):

   a. $[He]2s^{2}2p^{5}$
   b. $[Ar]3d^{10}4s^{1}$
   c. $[Kr]5s^{1}$

Answer

1. a. *p* block, second period, Group 17, halogens, fluorine, nonmetal, high reactivity
   b. *d* block, fourth period, Group 11, transition elements, copper, metal, low reactivity
   c. *s* block, fifth period, Group 1, alkali metals, rubidium, metal, high reactivity

SECTION REVIEW

1. Into what four blocks can the periodic table be divided to illustrate the relationship between the elements' electron configurations and their placement in the periodic table?
2. What name is given to each of the following groups of elements on the periodic table:
   a. Group 1
   b. Group 2
   c. Groups 3–12
   d. Group 17
   e. Group 18
3. What are the relationships between group configuration and group number for elements in the *s*, *p*, and *d* blocks?
4. Without looking at the periodic table, write the outer electron configuration for the Group 15 element in the fourth period.
5. Without looking at the periodic table, identify the period, block, and group of the element with the electron configuration $[Ar]3d^{7}4s^{2}$.

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SECTION 5-3

OBJECTIVES

- Define *atomic* and *ionic radii, ionization energy, electron affinity,* and *electronegativity.*
- Compare the periodic trends of atomic radii, ionization energy, and electronegativity, and state the reasons for these variations.
- Define *valence electrons,* and state how many are present in atoms of each main-group element.
- Compare the atomic radii, ionization energies, and electronegativities of the *d*-block elements with those of the main-group elements.

Electron Configuration and Periodic Properties

So far, you have learned that the elements are arranged in the periodic table according to their atomic number and that there is a rough correlation between the arrangement of the elements and their electron configurations. In this section, the relationship between the periodic law and electron configurations will be further explored.

Atomic Radii

Ideally, the size of an atom is defined by the edge of its orbital. However, this boundary is fuzzy and varies under different conditions. Therefore, to estimate the size of an atom, the conditions under which the atom exists must be specified. One way to express an atom's radius is to measure the distance between the nuclei of two identical atoms that are chemically bonded together, then divide this distance by two. As illustrated in Figure 5-12, **atomic radius** *may be defined as one-half the distance between the nuclei of identical atoms that are bonded together.*

Period Trends

Figure 5-13 gives the atomic radii of the elements and Figure 5-14 presents this information graphically. Note that there is a gradual decrease in atomic radii across the second period from lithium, Li, to neon, Ne.

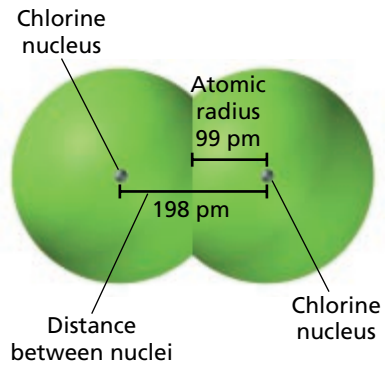

FIGURE 5-12 One method of determining atomic radius is to measure the distance between the nuclei of two identical atoms that are bonded together in an element or compound, then divide this distance by two. The atomic radius of a chlorine atom, for example, is 99 picometers (pm).

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Periodic Table of Atomic Radii (pm)

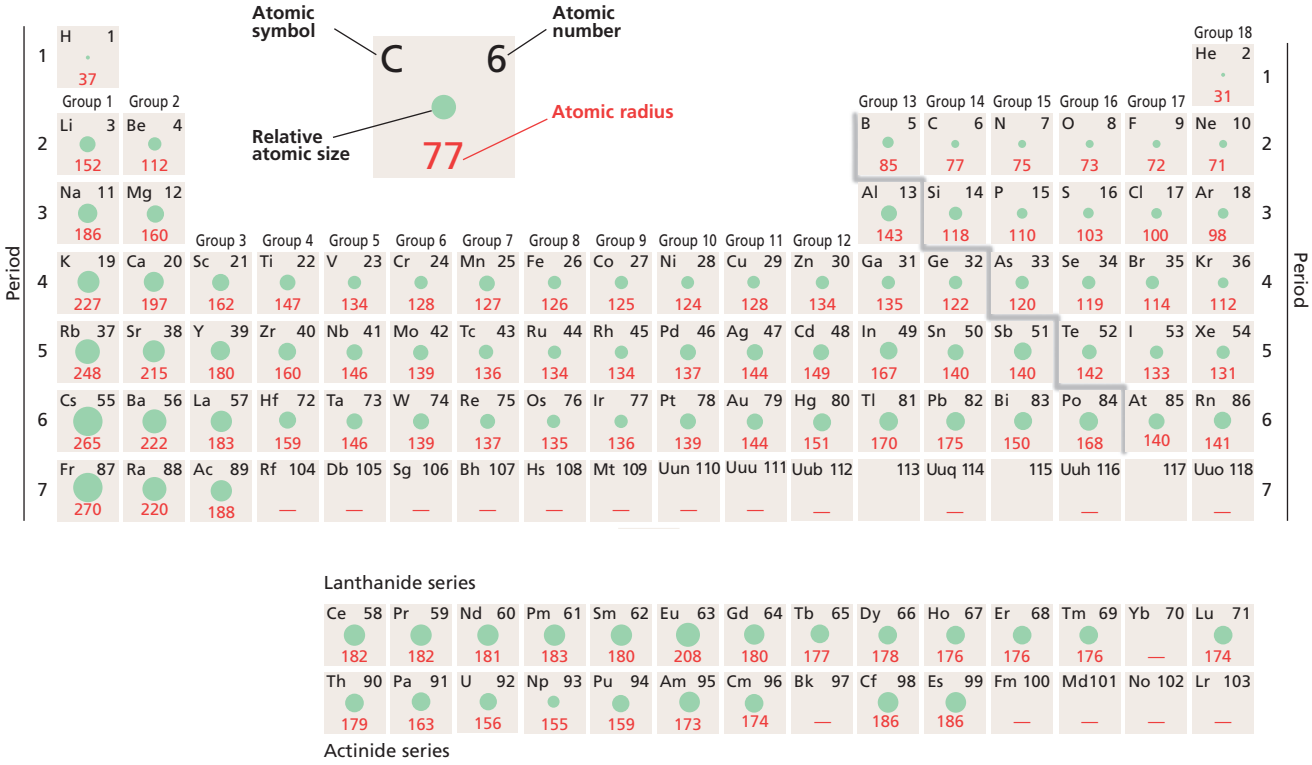

FIGURE 5-13 Atomic radii decrease from left to right across a period and increase down a group.

The trend to smaller atoms across a period is caused by the increasing positive charge of the nucleus. As electrons add to *s* and *p* sublevels in the same main energy level, they are gradually pulled closer to the more highly charged nucleus. This increased pull results in a decrease in atomic radii. The attraction of the nucleus is somewhat offset by repulsion among the increased number of electrons in the same outer energy level. As a result, the difference in radii between neighboring atoms in each period grows smaller, as shown in Figure 5-13.

Group Trends

Examine the atomic radii of the Group 1 elements in Figure 5-13. Notice that the radii of the elements increase as you read down the group. As electrons occupy sublevels in successively higher main energy levels located farther from the nucleus, the sizes of the atoms increase. *In general, the atomic radii of the main-group elements increase down a group*.

Now examine the radii of the Group 13 elements. Although gallium, Ga, follows aluminum, Al, it has a slightly smaller atomic radius than does aluminum. This is because gallium, unlike aluminum, is preceded in its period by the 10 *d*-block elements. The expected increase in gallium's radius caused by the filling of the fourth main-energy level is outweighed by a shrinking of the electron cloud caused by a nuclear charge that is considerably higher than that of aluminum.

CHEMISTRY INTERACTIVE TUTOR
Module 3: Periodic Properties

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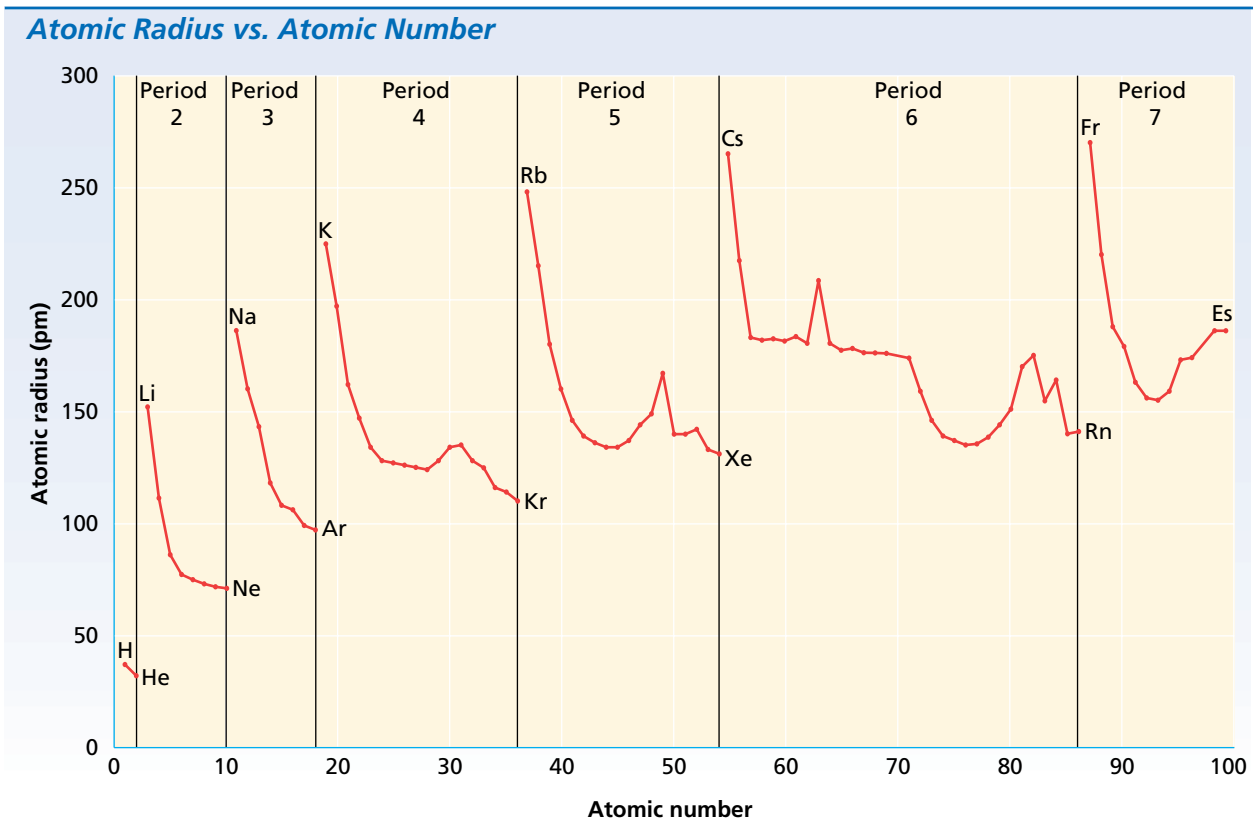

FIGURE 5-14 The plot of atomic radius versus atomic number shows period and group trends.

SAMPLE PROBLEM 5-5

a. Of the elements magnesium, Mg, chlorine, Cl, sodium, Na, and phosphorus, P, which has the largest atomic radius? Explain your answer in terms of trends in the periodic table.

b. Of the elements calcium, Ca, beryllium, Be, barium, Ba, and strontium, Sr, which has the largest atomic radius? Explain your answer in terms of trends in the periodic table.

SOLUTION

a. All of the elements are in the third period. Of the four, sodium has the lowest atomic number and is the first element in the period. Therefore, sodium has the largest atomic radius because atomic radii decrease across a period.

b. All of the elements are in Group 2. Of the four, barium has the highest atomic number and is farthest down the group. Therefore, barium has the largest atomic radius because atomic radii increase down a group.

PRACTICE

1. Of the elements Li, O, C, and F, identify the one with the largest atomic radius and the one with the smallest atomic radius. *Answer* Li, F

2. Of the elements Br, At, F, I, and Cl, identify the one with the smallest atomic radius and the one with the largest atomic radius. *Answer* F, At

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Ionization Energy

An electron can be removed from an atom if enough energy is supplied. Using A as a symbol for an atom of any element, the process can be expressed as follows.

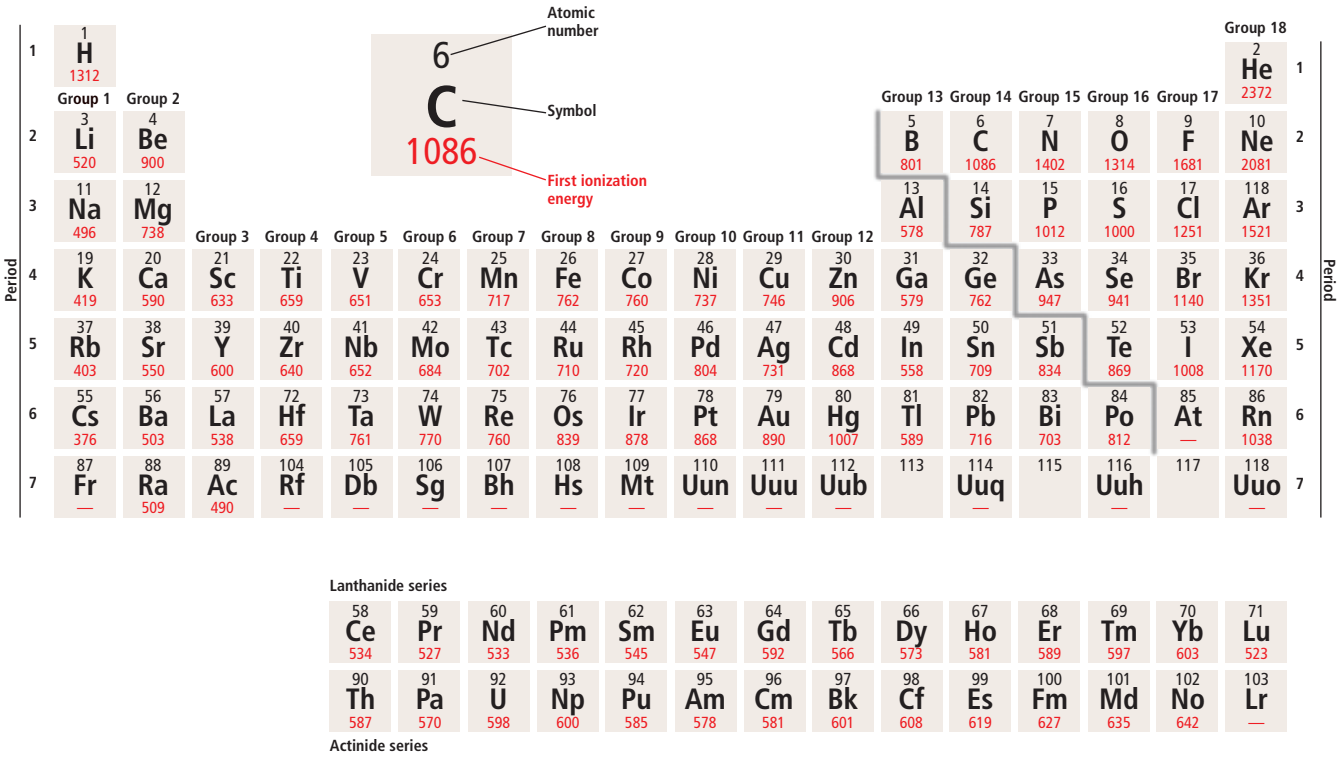
$$A + \text{energy} \rightarrow A^+ + e^-$$

The A^+ represents an ion of element A with a single positive charge, referred to as a 1+ ion. *An* **ion** *is an atom or group of bonded atoms that has a positive or negative charge.* Sodium, for example, forms an Na^+ ion. *Any process that results in the formation of an ion is referred to as* **ionization.**

To compare the ease with which atoms of different elements give up electrons, chemists compare ionization energies. *The energy required to remove one electron from a neutral atom of an element is the* **ionization energy, *IE*** *(or first ionization energy, IE_1).* To avoid the influence of nearby atoms, measurements of ionization energies are made on isolated atoms in the gas phase. Figure 5-15 gives the first ionization energies for the elements in kilojoules per mole (kJ/mol). Figure 5-16 presents this information graphically.

FIGURE 5-15 In general, first ionization energies increase across a period and decrease down a group.

Periodic Table of Ionization Energies (kJ/mol)



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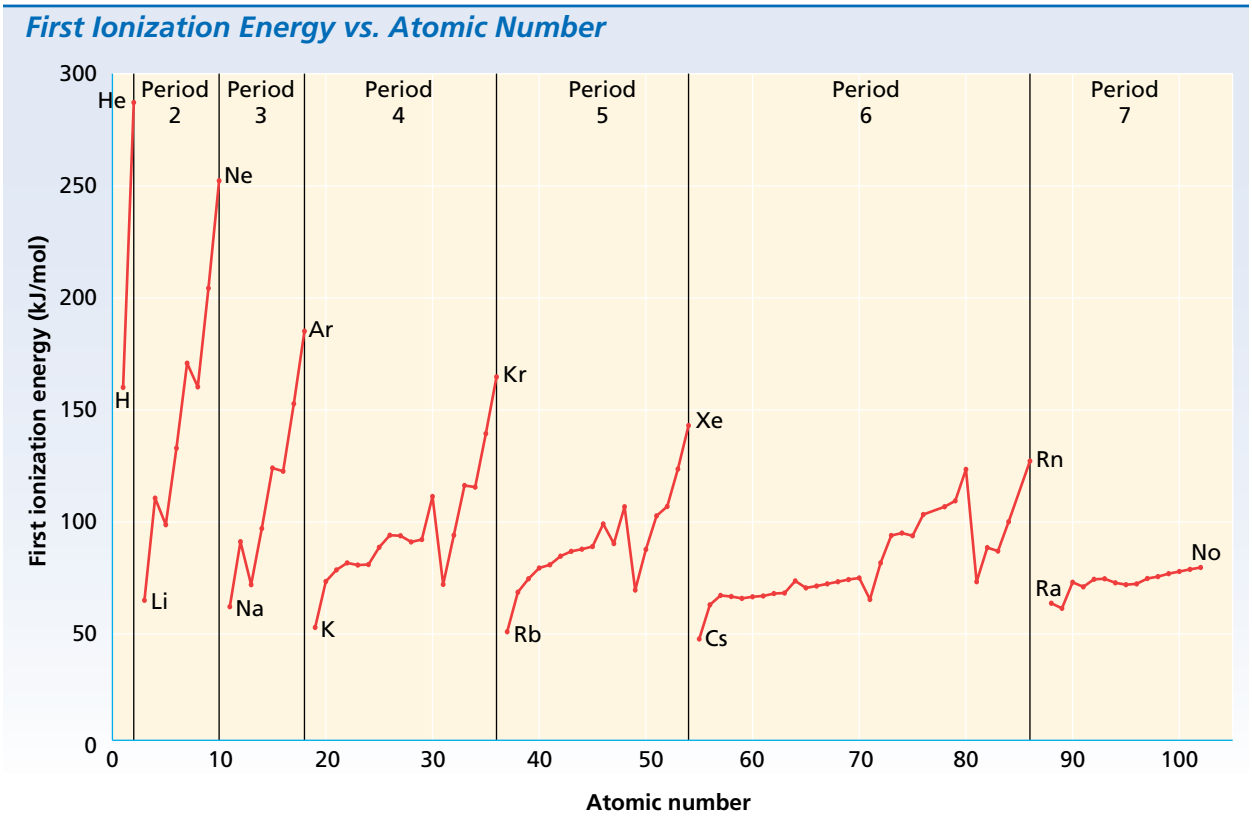

FIGURE 5-16 Plot of first ionization energy, IE_1, versus atomic number. As atomic number increases, both the period and the group trends become less pronounced.

Period Trends

In Figures 5-15 and 5-16, examine the ionization energies for the first and last elements in each period. You can see that the Group 1 metals have the lowest first ionization energies in their respective periods. Therefore, they lose electrons most easily. This ease of electron loss is a major reason for the high reactivity of the Group 1 (alkali) metals. The Group 18 elements, the noble gases, have the highest ionization energies. They do not lose electrons easily. The low reactivity of the noble gases is partly based on this difficulty of electron removal.

In general, ionization energies of the main-group elements increase across each period. This increase is caused by increasing nuclear charge. A higher charge more strongly attracts electrons in the same energy level. Increasing nuclear charge is responsible for both increasing ionization energy and decreasing radii across the periods. Note that, in general, nonmetals have higher ionization energies than metals do. In each period, the element of Group 1 has the lowest ionization energy and the element of Group 18 has the highest ionization energy.

Group Trends

Among the main-group elements, ionization energies generally decrease down the groups. Electrons removed from atoms of each succeeding element in a group are in higher energy levels, farther from the nucleus. Therefore, they are removed more easily. Also, as atomic number

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increases going down a group, more electrons lie between the nucleus and the electrons in the highest occupied energy levels. This partially shields the outer electrons from the effect of the nuclear charge. Together, these influences overcome the attraction of the electrons to the increasing nuclear charge.

Removing Electrons from Positive Ions

With sufficient energy, electrons can be removed from positive ions as well as from neutral atoms. The energies for removal of additional electrons from an atom are referred to as *the second ionization energy* (IE_2), *third ionization energy* (IE_3), and so on.

Table 5-3 shows the first five ionization energies for the elements of the first, second, and third periods. You can see that the second ionization energy is always higher than the first, the third is always higher than the second, and so on. This is because as electrons are removed in successive ionizations, fewer electrons remain within the atom to shield the attractive force of the nucleus. *Thus, each successive electron removed from an ion feels an increasingly stronger effective nuclear charge (the nuclear charge minus the electron shielding).*

The first ionization energies in Table 5-3 show that removing a single electron from an atom of a Group 18 element is more difficult than removing an electron from atoms of other elements in the same period. This special stability of the noble-gas configuration also applies to ions that have noble-gas configurations. Notice in Table 5-3 the large increases between the first and second ionization energies of lithium, Li, and between the second and third ionization energies of beryllium, Be. Even larger increases in ionization energy exist between the third and

TABLE 5-3 *Ionization Energies (in kJ/mol) for Elements of Periods 1–3*

	Period 1		Period 2							
	H	He	Li	Be	B	C	N	O	F	Ne
IE_1	1312	**2372**	520	900	801	1086	1402	1314	1681	2081
IE_2		5250	**7298**	1757	2427	2353	2856	3388	3374	3952
IE_3			11 815	**14 849**	3660	4621	4578	5300	6050	6122
IE_4				21 007	**25 026**	6223	7475	7469	8408	9370
IE_5					32 827	**37 830**	9445	10 990	11 023	12 178
			Period 3							
			Na	Mg	Al	Si	P	S	Cl	Ar
IE_1			496	738	578	787	1012	1000	1251	1521
IE_2			**4562**	1451	1817	1577	1903	2251	2297	2666
IE_3			6912	**7733**	2745	3232	2912	3361	3822	3931
IE_4			9544	10 540	**11 578**	4356	4957	4564	5158	5771
IE_5			13 353	13 628	14 831	**16 091**	6274	7013	6540	7238

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fourth ionization energies of boron, B, and between the fourth and fifth ionization energies of carbon, C. In each case, the jump in ionization energy occurs when an ion assumes a noble-gas configuration. For example, the removal of one electron from a lithium atom ([He]$2s^1$) leaves the helium noble-gas configuration. The removal of four electrons from a carbon atom ([He]$2s^2 2p^2$) also leaves the helium configuration. A bigger table would show that this trend continues across the entire periodic system.

SAMPLE PROBLEM 5-6

Consider two main-group elements A and B. Element A has a first ionization energy of 419 kJ/mol. Element B has a first ionization energy of 1000 kJ/mol. For each element, decide if it is more likely to be in the *s* block or *p* block. Which element is more likely to form a positive ion?

SOLUTION

Element A has a very low ionization energy, meaning that atoms of A lose electrons easily. Therefore, element A is most likely to be a metal of the *s* block because ionization energies increase across the periods. Element B has a very high ionization energy, meaning that atoms of B lose electrons with difficulty. We would expect element B to lie at the end of a period in the *p* block. Element A is more likely to form a positive ion because it has a much lower ionization energy than does element B.

PRACTICE

1. Consider the four hypothetical main-group elements Q, R, T, and X with the outer electron configurations indicated below. Then answer the questions that follow.

Q: $3s^2 3p^5$ R: $3s^1$ T: $4d^{10} 5s^2 5p^5$ X: $4d^{10} 5s^2 5p^1$

a. Identify the block location of each hypothetical main-group element.

b. Which of these elements are in the same period? Which are in the same group?

c. Which element would you expect to have the highest first ionization energy? Which would have the lowest first ionization energy?

d. Which element would you expect to have the highest second ionization energy?

e. Which of the elements is most likely to form a 1+ ion?

Answer

1. a. Q is in the *p* block, R is in the *s* block, T is in the *p* block, and X is in the *p* block.

b. Q and R, and X and T are in the same period. Q and T are in the same group.

c. Q would have the highest ionization energy, and R would have the lowest.

d. R

e. R

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Electron Affinity

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Neutral atoms can also acquire electrons. *The energy change that occurs when an electron is acquired by a neutral atom is called the atom's* **electron affinity.** Most atoms release energy when they acquire an electron.

$$A + e^- \longrightarrow A^- + \text{energy}$$

In this book, the quantity of energy released is represented by a negative number. On the other hand, some atoms must be "forced" to gain an electron by the addition of energy.

$$A + e^- + \text{energy} \longrightarrow A^-$$

The quantity of energy absorbed is represented by a positive number. An ion produced in this way will be unstable and will lose the added electron spontaneously.

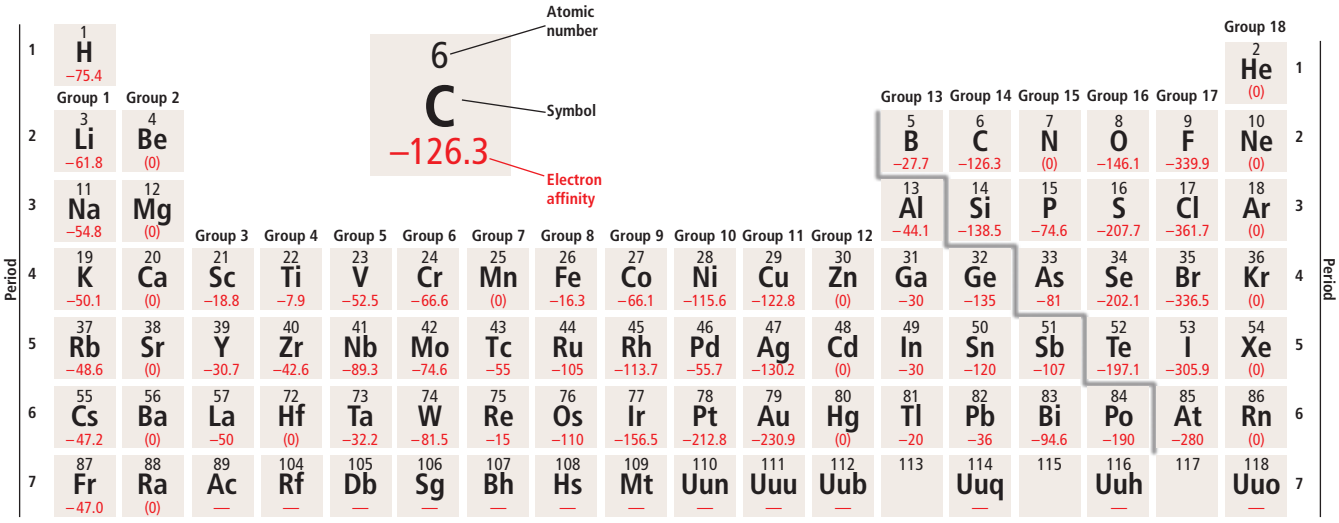
Figure 5-17 shows the electron affinity in kilojoules per mole for the elements. Figure 5-18 presents these data graphically.

Period Trends

Among the elements of each period, the halogens (Group 17) gain electrons most readily. This is indicated in Figure 5-17 by the large negative values of halogens' electron affinities. The ease with which halogen atoms gain electrons is a major reason for the high reactivities of the Group 17 elements. In general, as electrons add to the same *p* sublevel of atoms with increasing nuclear charge, electron affinities become more negative across each period within the *p* block. An exception to this trend occurs between Groups 14 and 15. Compare the electron affinities of carbon ([He]$2s^2 2p^2$) and nitrogen ([He]$2s^2 2p^3$). Adding an electron to a carbon atom gives a half-filled *p* sublevel. This occurs much more easily

FIGURE 5-17 The values listed in parentheses in this periodic table of electron affinities are approximate. Electron affinity is estimated to be –50 kJ/mol for each of the lanthanides and 0 kJ/mol for each of the actinides.

Periodic Table of Electron Affinities (kJ/mol)



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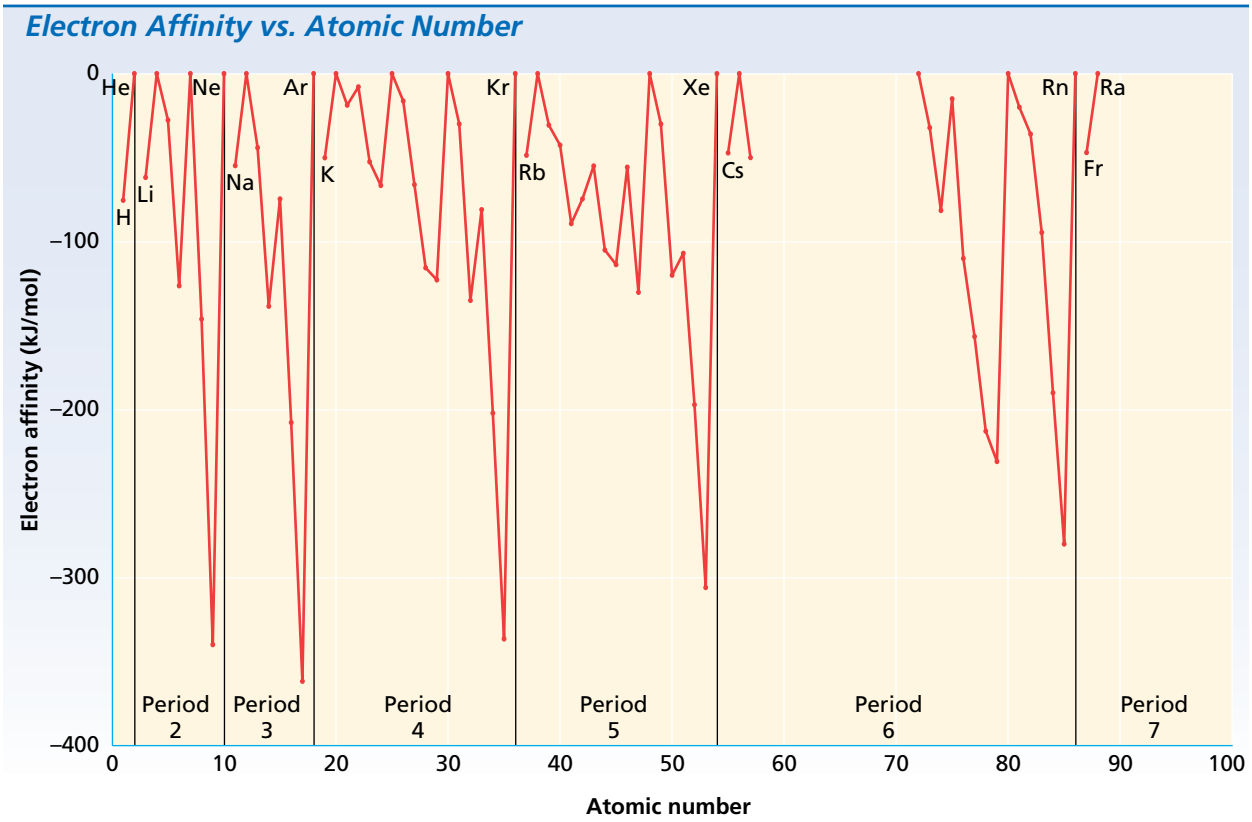

FIGURE 5-18 The plot of electron affinity versus atomic number shows that most atoms release energy when they acquire an electron, as indicated by negative values.

than forcing an electron to pair with another electron in an orbital of the already half-filled *p* sublevel of a nitrogen atom.

Group Trends

Trends for electron affinities within groups are not as regular as trends for ionization energies. As a general rule, electrons add with greater difficulty down a group. This pattern is a result of two competing factors. The first is a slight increase in effective nuclear charge down a group, which increases electron affinities. The second is an increase in atomic radius down a group, which decreases electron affinities. In general, the size effect predominates. But there are exceptions, especially among the heavy transition metals, which tend to be the same size or even decrease in radius down a group.

Adding Electrons to Negative Ions

For an isolated ion in the gas phase, it is always more difficult to add a second electron to an already negatively charged ion. Therefore, second electron affinities are all positive. Certain *p*-block nonmetals tend to form negative ions that have noble gas configurations. The halogens do so by adding one electron. For example, chlorine has the configuration $[Ne]3s^23p^5$. An atom of chlorine achieves the configuration of the noble gas argon by adding an electron to form the ion Cl^- ($[Ne]3s^23p^6$). Adding another electron is so difficult that Cl^{2-} never occurs. Atoms of

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Group 16 elements are present in many compounds as 2– ions. For example, oxygen ($[He]2s^22p^4$) achieves the configuration of the noble gas neon by adding two electrons to form the ion O^{2-}($[He]2s^22p^6$). Nitrogen achieves a neon configuration by adding three electrons to form the ion N^{3-}.

Ionic Radii

Figure 5-19 shows the radii of some of the most common ions of the elements. Positive and negative ions have specific names.

A positive ion is known as a **cation.** The formation of a cation by the loss of one or more electrons always leads to a decrease in atomic radius because the removal of the highest-energy-level electrons results in a smaller electron cloud. Also, the remaining electrons are drawn closer to the nucleus by its unbalanced positive charge.

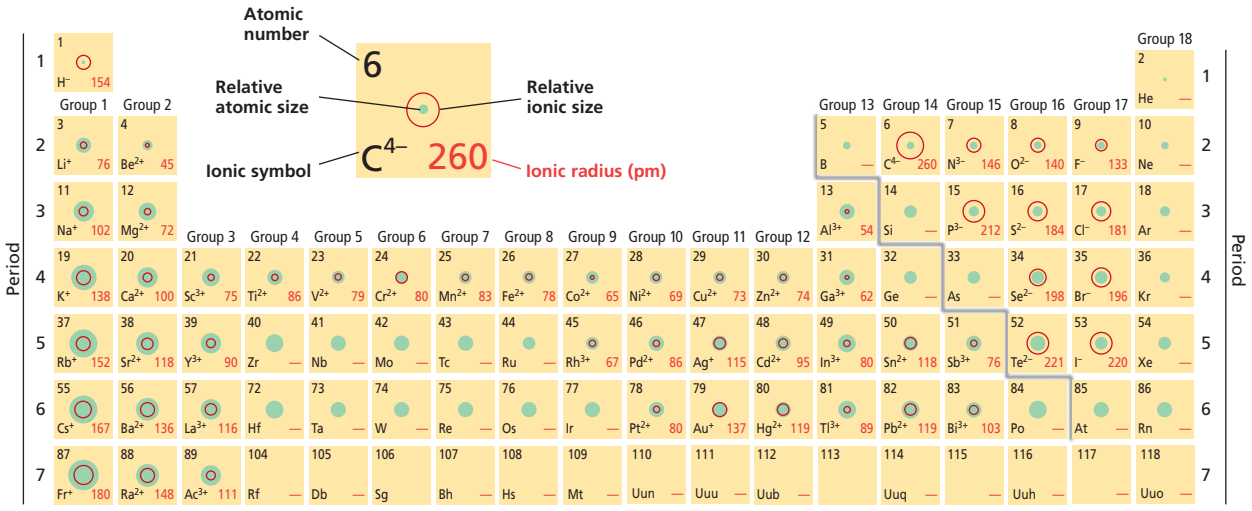
A negative ion is known as an **anion.** The formation of an anion by the addition of one or more electrons always leads to an increase in atomic radius. This is because the total positive charge of the nucleus remains unchanged when an electron is added to an atom or an ion. So the electrons are not drawn to the nucleus as strongly as they were before the addition of the extra electron. The electron cloud also spreads out because of greater repulsion between the increased number of electrons.

Period Trends

Within each period of the periodic table, the metals at the left tend to form cations and the nonmetals at the upper right tend to form anions. Cationic radii decrease across a period because the electron cloud shrinks due to the increasing nuclear charge acting on the electrons in

FIGURE 5-19 The ionic radii of the ions most common in chemical compounds are shown. Cations are smaller and anions are larger than the atoms from which they are formed.

Periodic Table of Ionic Radii (pm)



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the same main energy level. Starting with Group 15, in which atoms assume stable noble-gas configurations by gaining three electrons, anions are more common than cations. Anionic radii decrease across each period for the elements in Groups 15–18. The reasons for this trend are the same as the reasons that cationic radii decrease from left to right across a period.

Group Trends

As they are in atoms, the outer electrons in both cations and anions are in higher energy levels as one reads down a group. Therefore, just as there is a gradual increase of atomic radii down a group, there is also a gradual increase of ionic radii.

Valence Electrons

Chemical compounds form because electrons are lost, gained, or shared between atoms. The electrons that interact in this manner are those in the highest energy levels. These are the electrons most subject to the influence of nearby atoms or ions. *The electrons available to be lost, gained, or shared in the formation of chemical compounds are referred to as* **valence electrons.** Valence electrons are often located in incompletely filled main-energy levels. For example, the electron lost from the 3*s* sublevel of Na to form Na^+ is a valence electron.

For main-group elements, the valence electrons are the electrons in the outermost *s* and *p* sublevels. The inner electrons are in filled energy levels and are held too tightly by the nucleus to be involved in compound formation. The Group 1 and Group 2 elements have one and two valence electrons, respectively, as shown in Table 5-4. The elements of Groups 13–18 have a number of valence electrons equal to the group number minus 10. In some cases, both the *s* and *p* sublevel valence electrons of the *p*-block elements are involved in compound formation. In other cases, only the electrons from the *p* sublevel are involved.

TABLE 5-4 *Valence Electrons in Main-Group Elements*

Group number	Group configuration	Number of valence electrons
1	ns^1	1
2	ns^2	2
13	ns^2p^1	3
14	ns^2p^2	4
15	ns^2p^3	5
16	ns^2p^4	6
17	ns^2p^5	7
18	ns^2p^6	8

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Electronegativity

Valence electrons hold atoms together in chemical compounds. In many compounds, the negative charge of the valence electrons is concentrated closer to one atom than to another. This uneven concentration of charge has a significant effect on the chemical properties of a compound. It is therefore useful to have a measure of how strongly one atom attracts the electrons of another atom within a compound.

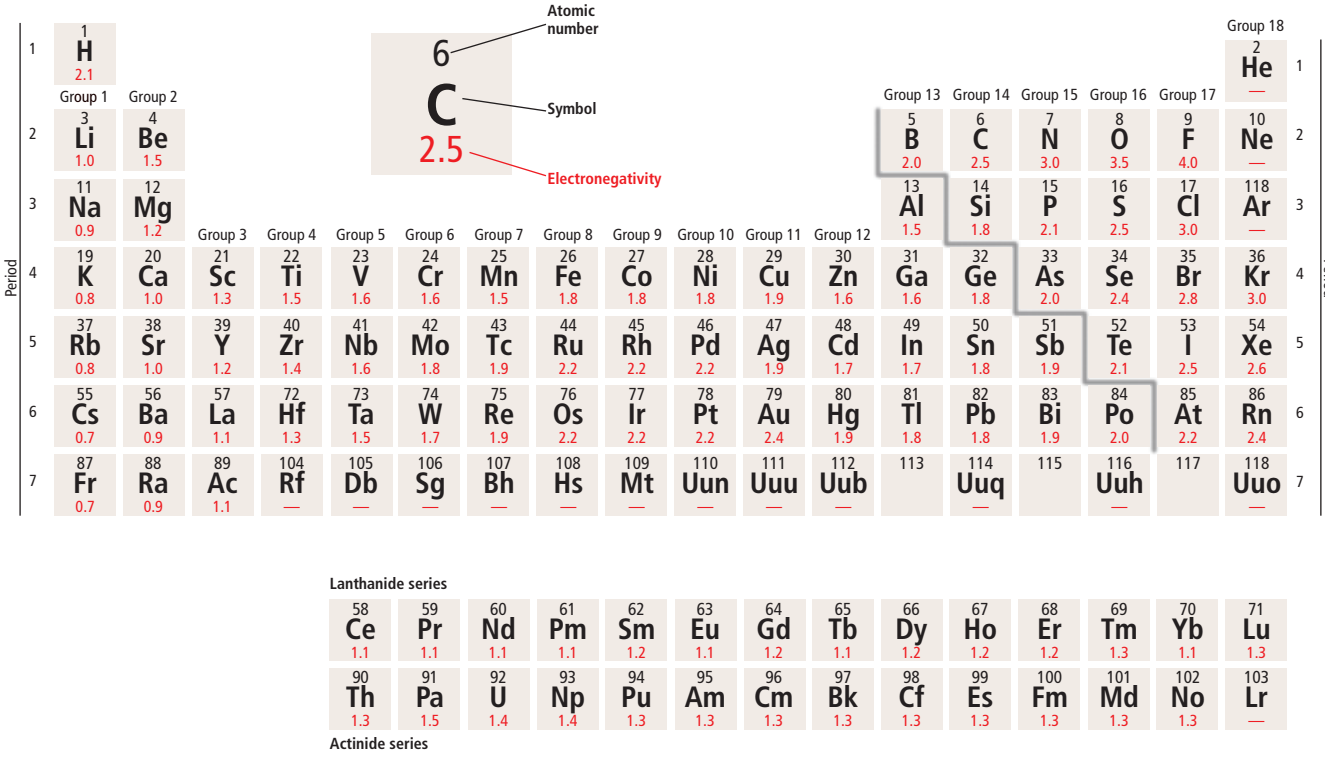
Linus Pauling, one of America's most famous chemists, devised a scale of numerical values reflecting the tendency of an atom to attract electrons. **Electronegativity** *is a measure of the ability of an atom in a chemical compound to attract electrons.* The most electronegative element, fluorine, is arbitrarily assigned an electronegativity value of four. Values for the other elements are then calculated in relation to this value.

Period Trends

As shown in Figure 5–20, electronegativities tend to increase across each period, although there are exceptions. The alkali and alkaline-earth metals are the least electronegative elements. In compounds, their atoms have a low attraction for electrons. Nitrogen, oxygen, and the halogens are the most electronegative elements. Their atoms attract electrons strongly in compounds. *Electronegativities tend to either decrease down a group or*

FIGURE 5-20 Shown are the electronegativities of the elements according to the Pauling scale. The most-electronegative elements are located in the upper right of the *p* block. The least-electronegative elements are located in the lower left of the *s* block.

Periodic Table of Electronegativities



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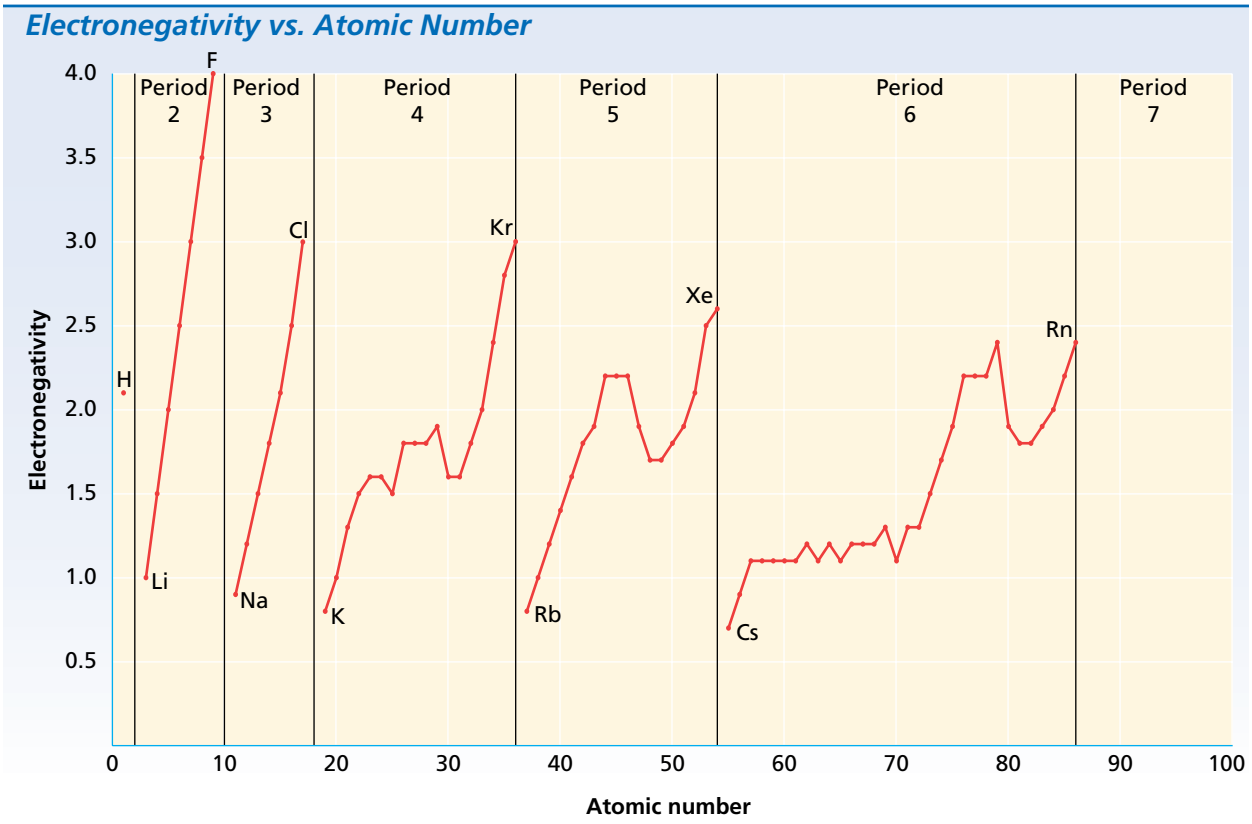

FIGURE 5-21 The plot shows electronegativity versus atomic number for Periods 1–6.

remain about the same. The noble gases are unusual in that some of them do not form compounds and therefore cannot be assigned electronegativities. When a noble gas does form a compound, its electronegativity is rather high, similar to the values for the halogens. The combination of the period and group trends in electronegativity results in the highest values belonging to the elements in the upper right of the periodic table. The lowest values belong to the elements in the lower left of the table. These trends are shown graphically in Figure 5-21.

SAMPLE PROBLEM 5-7

Among the elements gallium, Ga, bromine, Br, and calcium, Ca, which has the highest electronegativity? Explain why in terms of periodic trends.

SOLUTION

The elements are all in the fourth period. Bromine has the highest atomic number and is farthest to the right in the period. Therefore, it should have the highest electronegativity because electronegativity increases across the periods.

PRACTICE

1. Consider the five hypothetical main-group elements E, G, J, L, and M with the outer electron configurations shown at the top of page 153.

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$E = 2s^2 2p^5$ $G = 4d^{10} 5s^2 5p^5$ $J = 2s^2 2p^2$

$L = 5d^{10} 6s^2 6p^5$ $M = 2s^2 2p^4$

a. Identify the block location for each element. Then determine which elements are in the same period and which are in the same group.

b. Which element would you expect to have the highest electron affinity? Which would you expect to form a 1– ion? Which should have the highest electronegativity?

c. Compare the ionic radius of the typical ion formed by the element G with the radius of its neutral atom.

d. Which element(s) contains seven valence electrons?

Answer

1. a. All are in the *p* block. E, J, and M are in the same period, and E, G, and L are in the same group.

b. E should have the highest electron affinity; E, G, and L are most likely to form 1– ions; E should have the highest electronegativity.

c. The ionic radius would be larger.

d. E, G, and L

Periodic Properties of the *d*- and *f*-Block Elements

The properties of the *d*-block elements (which are all metals) vary less and with less regularity than those of the main-group elements. This trend is indicated by the curves in Figures 5-14 and 5-16, which flatten where the *d*-block elements fall in the middle of Periods 4–6.

Recall that atoms of the *d*-block elements contain from zero to two electrons in the *s* orbital of their highest occupied energy level and one to ten electrons in the *d* sublevel of the next-lower energy level. Therefore, electrons in both the *ns* sublevel and the $(n - 1)d$ sublevel are available to interact with their surroundings. As a result, electrons in the incompletely filled *d* sublevels are responsible for many characteristic properties of the *d*-block elements.

Atomic Radii

The atomic radii of the *d*-block elements generally decrease across the periods. However, this decrease is less than that for the main-group elements because the electrons added to the $(n - 1)d$ sublevel shield the outer electrons from the nucleus. Also, note in Figure 5-14 that the radii dip to a low and then increase slightly across each of the four periods that contain *d*-block elements. As the number of electrons in the *d* sublevel increases, the radii increase because of repulsion among the electrons.

In the sixth period, the *f*-block elements fall between lanthanum (Group 3) and hafnium (Group 4). Because of the increase in atomic number that occurs from lanthanum to hafnium, the atomic radius of hafnium is actually slightly less than that of zirconium, Zr, the element immediately above it. The radii of elements following hafnium in the sixth period vary with increasing atomic number in the usual manner.

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Ionization Energy

As they do for the main-group elements, ionization energies of the *d*-block and *f*-block elements generally increase across the periods. In contrast to the decrease down the main groups, however, the first ionization energies of the *d*-block elements generally increase down each group. This is because the electrons available for ionization in the outer *s* sublevels are less shielded from the increasing nuclear charge by electrons in the incomplete $(n - 1)d$ sublevels.

Ion Formation and Ionic Radii

The order in which electrons are removed from all atoms of the *d*-block and *f*-block elements is *exactly the reverse of the order given by the electron-configuration notation.* In other words, electrons in the highest occupied sublevel are always removed first. For the *d*-block elements, this means that although newly added electrons occupy the *d* sublevels, the first electrons to be removed are those in the outermost *s* sublevels. For example, iron, Fe, has the electron configuration $[Ar]3d^64s^2$. It loses a 4*s* electron first to form Fe^+ ($[Ar]3d^64s^1$). Fe^+ can then lose the second 4*s* electron to form Fe^{2+} ($[Ar]3d^6$). Fe^{2+} can then lose a 3*d* electron to form Fe^{3+} ($[Ar]3d^5$).

Most *d*-block elements commonly form 2+ ions in compounds. Some, such as iron and chromium, also commonly form 3+ ions. The Group 3 elements form only ions with a 3+ charge. Copper forms 1+ and 2+ ions, and silver usually forms only 1+ ions. As expected, the cations have smaller radii than the atoms do. Comparing 2+ ions across the periods shows a decrease in size that parallels the decrease in atomic radii.

Electronegativity

The *d*-block elements all have electronegativities between 1.1 and 2.54. Only the active metals of Groups 1 and 2 have lower electronegativities. The *d*-block elements also follow the general trend for electronegativity values to increase as radii decrease, and vice versa. The *f*-block elements all have similar electronegativities, which range from 1.1 to 1.5.

SECTION REVIEW

1. State the general period and group trends among main-group elements with respect to each of the following properties:

a. atomic radii
b. first ionization energy
c. electron affinity
d. ionic radii
e. electronegativity

2. Among the main-group elements, what is the relationship between group number and the number of valence electrons among group members?

3. a. In general, how do the periodic properties of the *d*-block elements compare with those of the main-group elements?
b. Explain the comparisons made in (a).

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CHAPTER 5 REVIEW

CHAPTER SUMMARY

5-1

- The periodic law states that the physical and chemical properties of the elements are periodic functions of their atomic numbers.
- The periodic table is an arrangement of the elements in order of their atomic numbers so that elements with similar properties fall in the same column.
- The columns in the periodic table are referred to as groups.

Vocabulary

actinide (126) lanthanide (126) periodic law (125) periodic table (125)

5-2

- The rows in the periodic table are called periods.
- Many chemical properties of the elements can be explained by the configurations of the elements' outermost electrons.
- The noble gases exhibit unique chemical stability because their highest occupied levels have an octet of electrons, ns^2np^6 (with the exception of helium, whose stability arises from its highest occupied level being completely filled with two electrons, $1s^2$).
- Based on the electron configurations of the elements, the periodic table can be divided into four blocks: the *s* block, the *p* block, the *d* block, and the *f* block.

Vocabulary

alkali metals (132) halogens (137) main-group elements (136) transition elements (134)
alkaline-earth metals (132)

5-3

- The groups and periods of the periodic table display general trends in the following properties of the elements: electron affinity, electronegativity, ionization energy, atomic radius, and ionic radius.
- The electrons in an atom that are available to be lost, gained, or shared in the formation of chemical compounds are referred to as valence electrons.
- In determining the electron configuration of an ion, the order in which electrons are removed from the atom is the reverse of the order given by the atom's electron-configuration notation.

Vocabulary

anion (149) electron affinity (147) ion (143) ionization energy (143)
atomic radius (140) electronegativity (151) ionization (143) valence electrons (150)
cation (149)

REVIEWING CONCEPTS

1. Describe the contributions made by the following scientists to the development of the periodic table:
a. Stanislao Cannizzaro
b. Dmitri Mendeleev
c. Henry Moseley (5-1)

2. State the periodic law. (5-1)

3. How is the periodic law demonstrated within the groups of the periodic table? (5-1)

4. a. How do the electron configurations within the same group of elements compare?
b. Why are the noble gases relatively unreactive? (5-2)

5. What determines the length of each period in the periodic table? (5-2)

6. What is the relationship between the electron configuration of an element and the period in which that element appears in the periodic table? (5-2)

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7. a. What information is provided by the specific block location of an element?
b. Identify, by number, the groups located within each of the four block areas. (5-2)

8. a. Which elements are designated as the alkali metals?
b. List four of their characteristic properties. (5-2)

9. a. Which elements are designated as the alkaline-earth metals?
b. How do their characteristic properties compare with those of the alkali metals? (5-2)

10. a. Write the usual group configuration notation for each *d*-block group.
b. How do the group numbers of those groups relate to the number of outer *s* and *d* electrons? (5-2)

11. What name is sometimes used to refer to the entire set of *d*-block elements? (5-2)

12. a. What types of elements make up the *p* block?
b. How do the properties of the *p*-block metals compare with those of the metals in the *s* and *d* blocks? (5-2)

13. a. Which elements are designated as the halogens?
b. List three of their characteristic properties. (5-2)

14. a. Which elements are metalloids?
b. Describe their characteristic properties. (5-2)

15. Which elements make up the *f* block in the periodic table? (5-2)

16. a. What are the main-group elements?
b. What trends can be observed across the various periods within the main-group elements? (5-2)

17. a. What is meant by atomic radius?
b. What trend is observed among the atomic radii of main-group elements across a period?
c. How can this trend be explained? (5-3)

18. a. What trend is observed among the atomic radii of main-group elements down a group?
b. How can this trend be explained? (5-3)

19. Define each of the following terms:
a. ion
b. ionization
c. first ionization energy
d. second ionization energy (5-3)

20. a. How do the first ionization energies of main-group elements vary across a period and down a group?
b. Explain the basis for each trend. (5-3)

21. a. What is electron affinity?
b. What signs are associated with electron affinity values, and what is the significance of each sign? (5-3)

22. a. Distinguish between a cation and an anion.
b. How does the size of each compare with the size of the neutral atom from which it is formed? (5-3)

23. a. What are valence electrons?
b. Where are such electrons located? (5-3)

24. For each of the following groups, indicate whether electrons are more likely to be lost or gained in compound formation and give the number of such electrons typically involved:
a. Group 1
b. Group 2
c. Group 13
d. Group 16
e. Group 17
f. Group 18 (5-3)

25. a. What is electronegativity?
b. Why is fluorine special in terms of electronegativity? (5-3)

26. Identify the most- and least-electronegative groups of elements in the periodic table. (5-3)

PROBLEMS

Electron Configuration and Periodic Properties

27. Write the noble-gas notation for the electron configuration of each of the following elements, and indicate the period in which each belongs:
a. Li
b. O
c. Cu
d. Br
e. Sn

28. Without looking at the periodic table, identify the period, block, and group in which the elements with the following electron configurations are located. (Hint: See Sample Problem 5-1.)
a. $[Ne]3s^2 3p^4$
b. $[Kr]4d^{10}5s^2 5p^2$
c. $[Xe]4f^{14}5d^{10}6s^2 6p^5$

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29. Based on the information given below, give the group, period, block, and identity of each element described. (Hint: See Sample Problem 5-2.)
a. $[He]2s^2$
b. $[Ne]3s^1$
c. $[Kr]5s^2$
d. $[Ar]4s^2$
e. $[Ar]3d^5 4s^1$

30. Without looking at the periodic table, write the expected outer electron configuration for each of the following elements. (Hint: See Sample Problem 5-3.)
a. Group 7, fourth period
b. Group 3, fifth period
c. Group 12, sixth period

31. Identify the block, period, group, group name (where appropriate), element name, element type, and relative reactivity for the elements with the following electron configurations. (Hint: See Sample Problem 5-4.)
a. $[Ne]3s^2 3p^1$
b. $[Ar]3d^{10} 4s^2 4p^6$
c. $[Kr]4d^{10} 5s^1$
d. $[Xe]4f^1 5d^1 6s^2$

Atomic Radius, Ionization, Electron Affinity, and Electronegativity

32. Of cesium, Cs, hafnium, Hf, and gold, Au, which element has the smallest atomic radius? Explain your answer in terms of trends in the periodic table. (Hint: see Sample Problem 5-5.)

33. a. Distinguish between the first, second, and third ionization energies of an atom.
b. How do the values of successive ionization energies compare?
c. Why does this occur?

34. Without looking at the electron affinity table, arrange the following elements in order of *decreasing* electron affinities: C, O, Li, Na, Rb, and F.

35. a. Without looking at the ionization energy table, arrange the following elements in order of decreasing first ionization energies: Li, O, C, K, Ne, and F.
b. Which of the elements listed in (a) would you expect to have the highest second ionization energy? Why?

36. a. Which of the following cations is least likely to form: Sr^{2+}, Al^{3+}, K^{2+}?
b. Which of the following anions is least likely to form: I^-, Cl^-, O^{2-}?

37. Which element is the most electronegative among C, N, O, Br, and S? Which group does it belong to? (Hint: See Sample Problem 5-7.)

38. The two ions K^+ and Ca^{2+} each have 18 electrons surrounding the nucleus. Which would you expect to have the smaller radius? Why?

MIXED REVIEW

39. Without looking at the periodic table, identify the period, block, and group in which each of the following elements is located:
a. $[Rn]7s^1$
b. $[Ar]3d^2 4s^2$
c. $[Kr]4d^{10} 5s^1$
d. $[Xe]4f^{14} 5d^9 6s^1$

40. a. Which elements are designated as the noble gases?
b. What is the most significant property of these elements?

41. Which of the following does not have a noble-gas configuration: Na^+, Rb^+, O^{2-}, Br^-, Ca^+, Al^{3+}, S^{2-}?

42. a. How many groups are in the periodic table?
b. How many periods are in the periodic table?
c. Which two blocks of the periodic table make up the main-group elements?

43. Write the noble-gas notation for the electron configuration of each of the following elements, and indicate the period and group in which each belongs:
a. Mg
b. P
c. Sc
d. Y

44. Use the periodic table to describe the chemical properties of the following elements:
a. fluorine, F
b. xenon, Xe
c. sodium, Na
d. gold, Au

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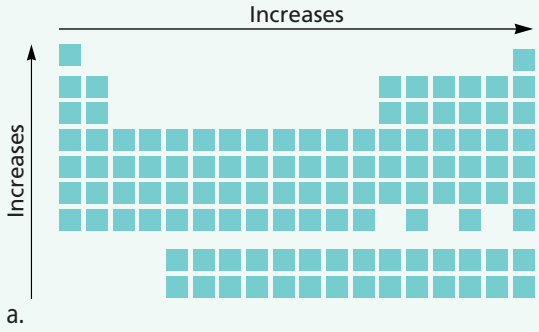
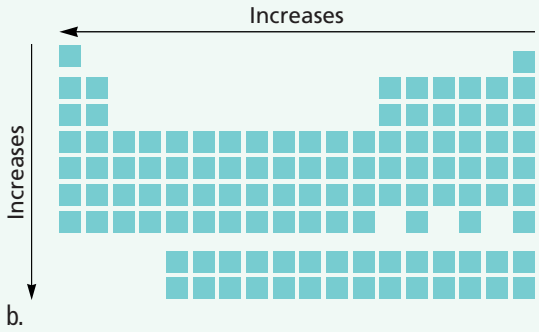
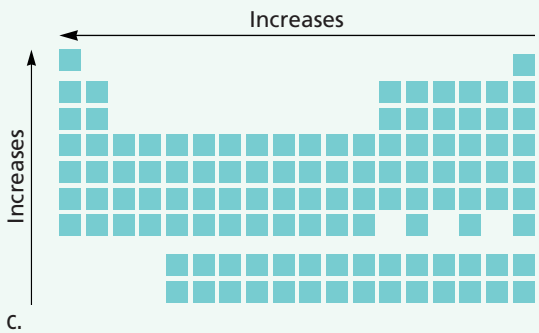
45. Identify which trends in the diagrams below describe atomic radius, ionization energy, electron affinity, and electronegativity.



a.



b.



c.

46. For each element listed below, determine the charge of the ion most likely to be formed and the identity of the noble gas whose electron configuration is thus achieved.

a. Li
b. Rb
c. O
d. F
e. Mg
f. Al
g. P
h. S
i. Br
j. Ba

47. Describe some differences between the *s*-block metals and the *d*-block metals.

48. Why do the halogens readily form 1– ions?

49. The electron configuration of argon differs from those of chlorine and potassium by one electron each. Compare the reactivity of these three elements.

CRITICAL THINKING

As a member on the newly inhabited space station Alpha, you are given the task of organizing information on newly discovered elements as it comes in from the laboratory. To date, five elements have been discovered and have been assigned names and symbols from the Greek alphabet. An analysis of the new elements has yielded the following data:

Element name	Atomic no.	Atomic mass	Properties
Epsilon ε	23	47.33	nonmetal, very reactive, produces a salt when combined with a metal, gaseous state
Beta β	13	27.01	metal, very reactive, soft solid, low melting point
Gamma γ	12	25.35	nonmetal, gaseous element, extremely unreactive
Delta Δ	4	7.98	nonmetal, very abundant, forms compounds with most other elements
Lambda Λ	9	16.17	metal, solid state, good conductor, high luster, hard and dense

50. Applying Models Using the data on the five new elements, create a periodic table based on their properties.

51. Predicting Outcomes Using your newly created periodic table, predict the atomic number of an element with an atomic mass of 11.29 that has nonmetallic properties and is very reactive.

52. Predicting Outcomes Predict the atomic number of an element having an atomic mass of 15.02 that exhibits metallic properties but is softer than lambda and harder than beta.

53. Analyzing Information Analyze your periodic table for periodic trends, and describe the trends that you identify.

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TECHNOLOGY & LEARNING

54. Graphing Calculator Graphing Atomic Radius vs. Atomic Number

The graphing calculator can run a program that graphs data such as atomic radius versus atomic number. Graphing the data within the different periods will allow you to discover trends. Begin by creating a table of data. Then use the program to plot the data.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data sets and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that after creating the lists, you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. Would you expect any atomic number to have an atomic radius of 20? Why or why not?

b. A relationship is considered a function if it can pass a vertical line test. That is, if a vertical line can be drawn anywhere on the graph and only pass through one point, the relationship is a function. Do either of these sets of data represent a function? If so, which one(s)?

c. How would you describe the graphical relationship between the atomic numbers and atomic radii?

HANDBOOK SEARCH

55. Review the boiling point and melting point data in the tables of the *Elements Handbook* (beginning on page 730). Make a list of the elements that exist as liquids or gases at the boiling point of water, 100°C.

56. Because transition metals have vacant *d* orbitals, they form a greater variety of colored compounds than do the metals of Groups 1 and 2. Review the section of the *Elements Handbook* on transition metals (pages 740–749) and answer the following:

a. What colors are exhibited by chromium in its common oxidation states?

b. What gems contain chromium impurities?

c. What colors are often associated with the following metal ions: copper, cadmium, cobalt, zinc, and nickel?

d. What transition elements are considered noble metals? What are the characteristics of a noble metal?

RESEARCH & WRITING

57. Prepare a report tracing the evolution of the current periodic table since 1900. Cite the chemists involved and their major contributions.

58. Write a report describing the contributions of Glenn Seaborg toward the discovery of many of the actinide elements.

ALTERNATIVE ASSESSMENT

59. Your teacher will give you an index card that identifies the electronegativity, ionization energy, and electron affinity of an element. Identify the element by analyzing these properties in relation to periodic trends.

60. Construct your own periodic table or obtain a poster that shows related objects, such as fruits or vegetables, in periodic arrangement. Describe the organization of the table and the trends it illustrates. Use this table to make predictions about your subject matter.

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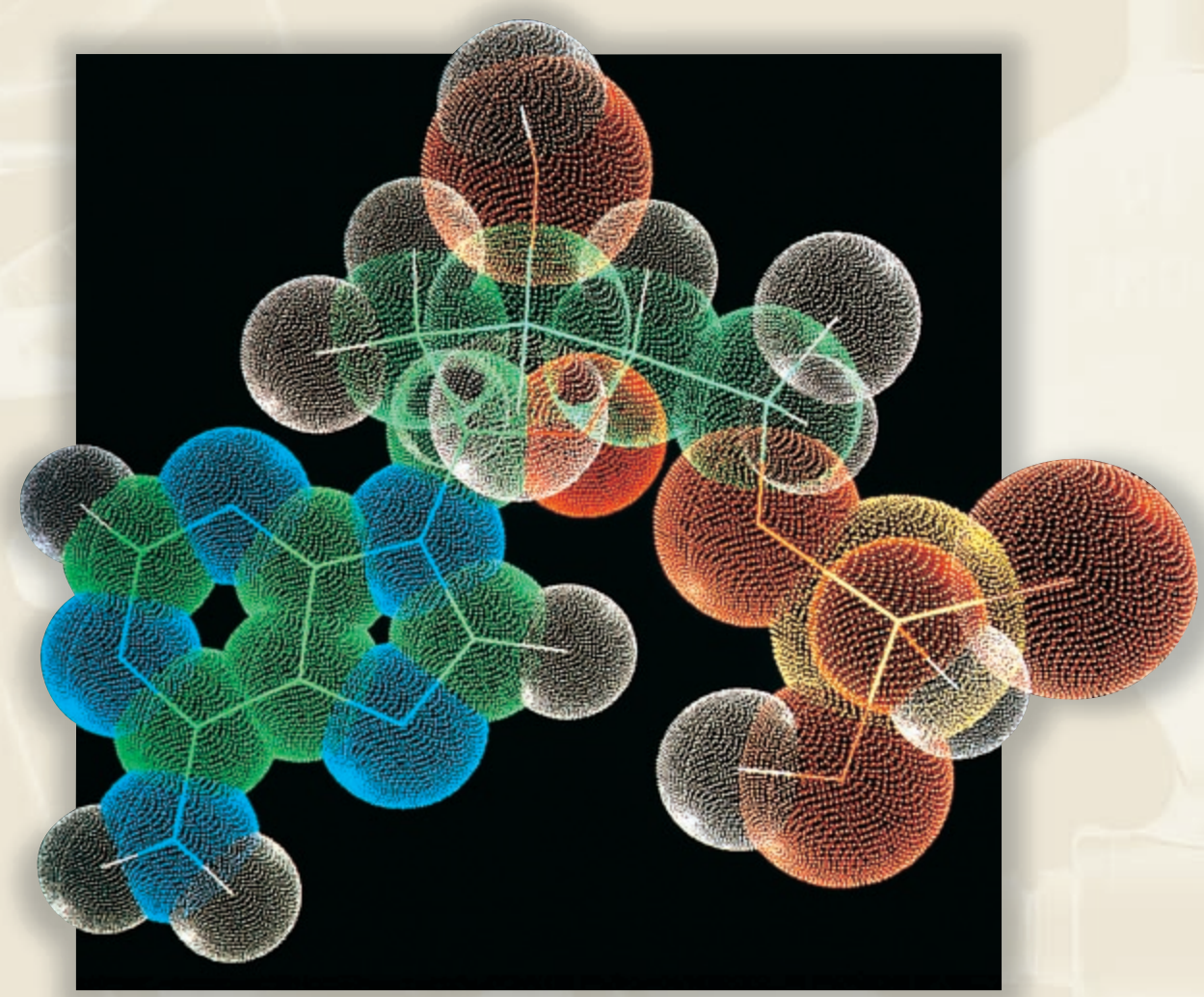
CHAPTER 6

Chemical Bonding



In nature, most atoms are joined to other atoms by chemical bonds.

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SECTION 6-1

Introduction to Chemical Bonding

Objectives

- Define *chemical bond.*
- Explain why most atoms form chemical bonds.
- Describe ionic and covalent bonding.
- Explain why most chemical bonding is neither purely ionic nor purely covalent.
- Classify bonding type according to electronegativity differences.

Atoms seldom exist as independent particles in nature. The oxygen you breathe, the water that makes up most of your body, and nearly all other substances are made up of combinations of atoms that are held together by chemical bonds. *A* **chemical bond** *is a mutual electrical attraction between the nuclei and valence electrons of different atoms that binds the atoms together.*

Why are most atoms chemically bonded to each other? As independent particles, they are at relatively high potential energy. Nature, however, favors arrangements in which potential energy is minimized. This means that most atoms are less stable existing by themselves than when they are combined. By bonding with each other, atoms decrease in potential energy, thereby creating more stable arrangements of matter.

Types of Chemical Bonding

When atoms bond, their valence electrons are redistributed in ways that make the atoms more stable. The way in which the electrons are redistributed determines the type of bonding. In Chapter 5, you read that main-group metals tend to lose electrons to form positive ions, or cations, and nonmetals tend to gain electrons to form negative ions, or anions. *Chemical bonding that results from the electrical attraction between large numbers of cations and anions is called* **ionic bonding.** In purely ionic bonding, atoms completely give up electrons to other atoms, as illustrated in Figure 6-1 on page 162. In contrast to atoms joined by ionic bonding, atoms joined by covalent bonding share electrons. **Covalent bonding** *results from the sharing of electron pairs between two atoms* (see Figure 6-1). In a purely covalent bond, the shared electrons are "owned" equally by the two bonded atoms.

Ionic or Covalent?

Bonding between atoms of different elements is rarely purely ionic or purely covalent. It usually falls somewhere between these two extremes, depending on how strongly the atoms of each element attract electrons. Recall that electronegativity is a measure of an atom's ability to attract electrons. The degree to which bonding between atoms of two elements

CHEMISTRY INTERACTIVE TUTOR

Module 4: Chemical Bonding

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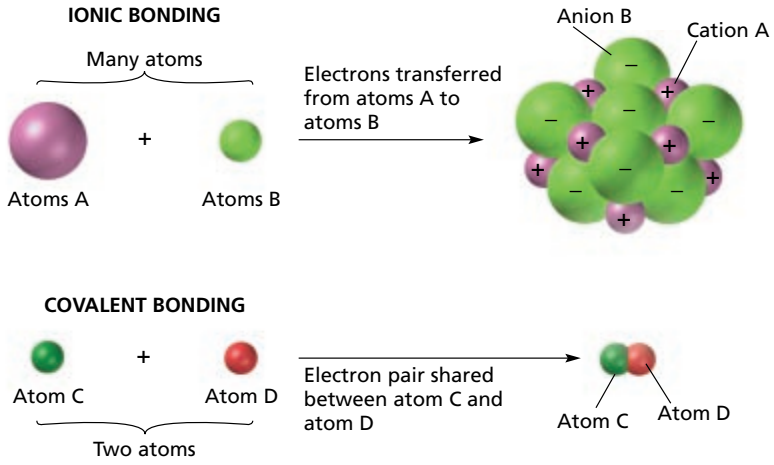

FIGURE 6-1 In ionic bonding, many atoms transfer electrons. The resulting positive and negative ions combine due to mutual electrical attraction. In covalent bonding, atoms share electron pairs to form independent molecules.

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is ionic or covalent can be estimated by calculating the difference in the elements' electronegativities (see Figure 6-2). For example, the electronegativity difference between fluorine, F, and cesium, Cs, is 4.0 – 0.7 = 3.3. (See Figure 5-20 on page 151 for a periodic table of electronegativity values.) So, according to Figure 6-2, cesium-fluorine bonding is ionic. The valence electrons are close to the highly electronegative fluorine atoms, causing the atoms to resemble anions, and far from the barely electronegative cesium atoms, which resemble cations.

Bonding between atoms with an electronegativity difference of 1.7 or less has an ionic character of 50% or less and is classified as covalent. Bonding between two atoms of the same element is completely covalent. Hydrogen, for example, exists in nature not as isolated atoms, but as pairs of atoms held together by covalent bonds. The hydrogen-hydrogen bond has 0% ionic character. It is a **nonpolar-covalent bond,** *a covalent bond in which the bonding electrons are shared equally by the bonded atoms, resulting in a balanced distribution of electrical charge.* Bonds having 0 to 5% ionic character, corresponding to electronegativity differences of roughly 0 to 0.3, are generally considered nonpolar-covalent bonds. In bonds with significantly different electronegativities, the electrons are more strongly attracted by the more-electronegative atom. *Such bonds are* **polar,** *meaning that they have an uneven distribution of charge.* Covalent bonds having 5 to 50% ionic character, corresponding to electronegativity differences of 0.3 to 1.7, are classified as polar. *A* **polar-covalent bond** *is a covalent bond in which the bonded atoms have an unequal attraction for the shared electrons.*

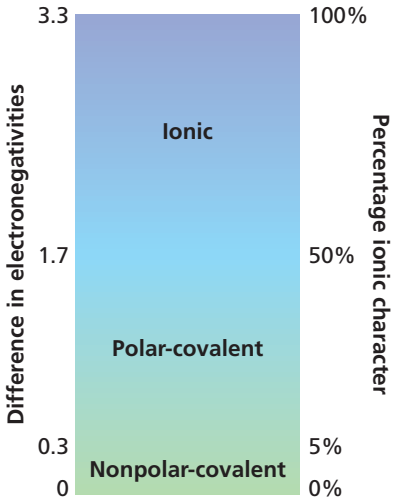

FIGURE 6-2 Differences in electronegativities reflect the character of bonding between elements. The electronegativity of the less-electronegative element is subtracted from that of the more-electronegative element. The greater the electronegativity difference, the more ionic is the bonding.

Nonpolar- and polar-covalent bonds are compared in Figure 6-3, which illustrates the electron density distribution in hydrogen-hydrogen and hydrogen-chlorine bonds. The electronegativity difference between chlorine and hydrogen is 3.0 – 2.1 = 0.9, indicating a polar-covalent bond. The electrons in this bond are closer to the more-electronegative chlorine atom than to the hydrogen atom, as indicated in Figure 6-3(b). Consequently, the chlorine end of the bond has a partial negative charge, indicated by the symbol δ–. The hydrogen end of the bond then has an equal partial positive charge, δ+.

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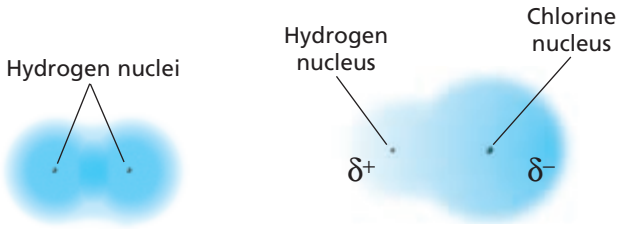

(a) Nonpolar-covalent bond **(b)** Polar-covalent bond

FIGURE 6-3 Comparison of the electron density in (a) a nonpolar, hydrogen-hydrogen bond and (b) a polar, hydrogen-chlorine bond. Because chlorine is more electronegative than hydrogen, the electron density in the hydrogen-chlorine bond is greater around the chlorine atom.

SAMPLE PROBLEM 6-1

Use electronegativity differences and Figure 6-2 to classify bonding between sulfur, S, and the following elements: hydrogen, H; cesium, Cs; and chlorine, Cl. In each pair, which atom will be more negative?

SOLUTION

From Figure 5-20 on page 151, we know that the electronegativity of sulfur is 2.5. The electronegativities of hydrogen, cesium, and chlorine are 2.1, 0.7, and 3.0, respectively. In each pair, the atom with the larger electronegativity will be the more-negative atom.

Bonding between sulfur and	Electronegativity difference	Bond type	More-negative atom
hydrogen	2.5 – 2.1 = 0.4	polar-covalent	sulfur
cesium	2.5 – 0.7 = 1.8	ionic	sulfur
chlorine	3.0 – 2.5 = 0.5	polar-covalent	chlorine

PRACTICE

Use electronegativity differences and Figure 6-2 to classify bonding between chlorine, Cl, and the following elements: calcium, Ca; oxygen, O; and bromine, Br. Indicate the more-negative atom in each pair.

Answer

Bonding between chlorine and	Electronegativity difference	Bond type	More-negative atom
calcium	3.0 – 1.0 = 2.0	ionic	chlorine
oxygen	3.5 – 3.0 = 0.5	polar-covalent	oxygen
bromine	3.0 – 2.8 = 0.2	nonpolar-covalent	chlorine

SECTION REVIEW

1. What is the main distinction between ionic and covalent bonding?
2. How is electronegativity used in determining the ionic or covalent character of the bonding between two elements?
3. What type of bonding would be expected between the following atoms?
   a. H and F
   b. Cu and S
   c. I and Br
4. List the three pairs of atoms referred to in the previous question in order of increasing ionic character of the bonding between them.

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SECTION 6-2

OBJECTIVES

- Define *molecule* and *molecular formula.*
- Explain the relationships between potential energy, distance between approaching atoms, bond length, and bond energy.
- State the octet rule.
- List the six basic steps used in writing Lewis structures.
- Explain how to determine Lewis structures for molecules containing single bonds, multiple bonds, or both.
- Explain why scientists use resonance structures to represent some molecules.

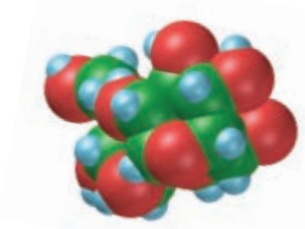
Covalent Bonding and Molecular Compounds

Many chemical compounds, including most of the chemicals that are in living things and are produced by living things, are composed of molecules. *A* **molecule** *is a neutral group of atoms that are held together by covalent bonds.* A single molecule of a chemical compound is an individual unit capable of existing on its own. It may consist of two or more atoms of the same element, as in oxygen, or of two or more different atoms, as in water or sugar (see Figure 6-4 below). *A chemical compound whose simplest units are molecules is called a* **molecular compound.**

The composition of a compound is given by its chemical formula. *A* **chemical formula** *indicates the relative numbers of atoms of each kind in a chemical compound by using atomic symbols and numerical subscripts.* The chemical formula of a molecular compound is referred to as a molecular formula. *A* **molecular formula** *shows the types and numbers of atoms combined in a single molecule of a molecular compound.* The molecular formula for water, for example, is H_2O, which reflects the fact that a single water molecule consists of one oxygen atom joined by separate covalent bonds to two hydrogen atoms. A molecule of oxygen, O_2, is an example of a diatomic molecule. *A* **diatomic molecule** *is a molecule containing only two atoms.*

(a) Water molecule, H_2O

(b) Oxygen molecule, O_2



(c) Sucrose molecule, $C_{12}H_{22}O_{11}$

FIGURE 6-4 The models for (a) water, (b) oxygen, and (c) sucrose, or table sugar, represent a few examples of the many molecular compounds in and around us. Atoms within molecules may form one or more covalent bonds.

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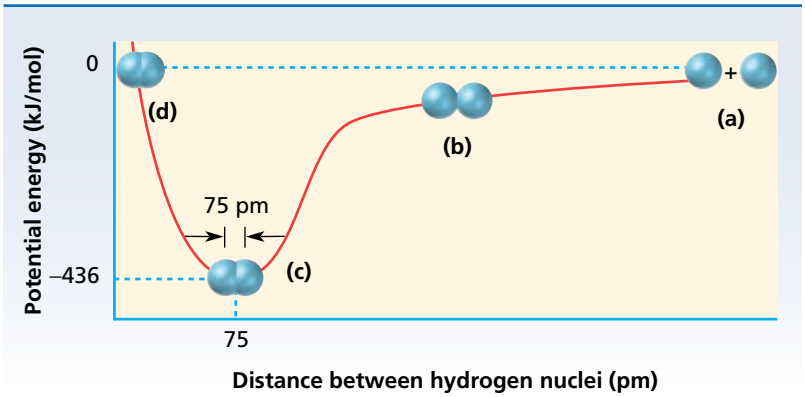

FIGURE 6-5 Potential energy changes during the formation of a hydrogen-hydrogen bond. (a) The separated hydrogen atoms do not affect each other. (b) Potential energy decreases as the atoms are drawn together by attractive forces. (c) Potential energy is at a minimum when attractive forces are balanced by repulsive forces. (d) Potential energy increases when repulsion between like charges outweighs attraction between opposite charges.

Formation of a Covalent Bond

As you read in Section 6-1, nature favors chemical bonding because most atoms are at lower potential energy when bonded to other atoms than they are at as independent particles. In the case of covalent bond formation, this idea is illustrated by a simple example, the formation of a hydrogen-hydrogen bond.

Picture two isolated hydrogen atoms separated by a distance large enough to prevent them from influencing each other. At this distance, the overall potential energy of the atoms is arbitrarily set at zero, as shown in part (a) of Figure 6-5.

Now consider what happens if the hydrogen atoms approach each other. Each atom has a nucleus containing a single positively charged proton. The nucleus of each atom is surrounded by a negatively charged electron in a spherical 1*s* orbital. As the atoms near each other, their charged particles begin to interact. As shown in Figure 6-6, the approaching nuclei and electrons are *attracted* to each other, which corresponds to a *decrease* in the total potential energy of the atoms. At the same time, the two nuclei *repel* each other and the two electrons *repel* each other, which results in an *increase* in potential energy.

The relative strength of attraction and repulsion between the charged particles depends on the distance separating the atoms. When the atoms first "see" each other, the electron-proton attraction is stronger than the electron-electron and proton-proton repulsions. Thus, the atoms are drawn to each other and their potential energy is lowered, as shown in part (b) of Figure 6-5.

The attractive force continues to dominate and the total potential energy continues to decrease until, eventually, a distance is reached at which the repulsion between the like charges equals the attraction of the opposite charges. This is shown in part (c) of Figure 6-5. At this point, which is represented by the bottom of the valley in the curve, potential energy is at a minimum and a stable hydrogen molecule forms. A closer approach of the atoms, shown in part (d) of Figure 6-5, results in a sharp rise in potential energy as repulsion becomes increasingly greater than attraction.

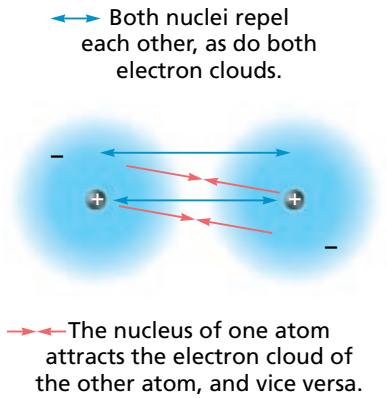
Both nuclei repel each other, as do both electron clouds.
–
+
+
–
The nucleus of one atom attracts the electron cloud of the other atom, and vice versa.

FIGURE 6-6 The arrows indicate the attractive and repulsive forces between the electrons (shown as electron clouds) and nuclei of two hydrogen atoms. Attraction between particles corresponds to a decrease in potential energy of the atoms, while repulsion corresponds to an increase.

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Ultrasonic Toxic-Waste Destroyer

Paints, pesticides, solvents, and sulfides—these are just a few components of the 600 million tons of toxic waste that flow out of America's factories every year. Much of this waste ends up in ground water, contaminating our streams and drinking water.

Eliminating hazardous waste is a constant challenge. Unfortunately, today's disposal methods often damage the environment as much as they help it. Incinerators burning certain waste, for example, produce dioxins, one of the most dangerous class of toxins known to man.

Finding new methods to destroy toxic waste is a puzzle. Michael Hoffmann, a professor of environmental chemistry at the California Institute of Technology, thinks that part of the solution lies in sound-wave technology.

According to Hoffmann, the key to eliminating certain chemical wastes from polluted water is a phenomenon called cavitation. Cavitation occurs when the pressure in water is made to fluctuate from slightly above to slightly below normal, causing bubbles. The bubbles are unstable and collapse, creating tiny areas of extremely high pressure and heat. The pressure inside a collapsing bubble can be 1000 times greater than normal, and the temperature reaches about 5000°C—just a bit cooler than the surface of the sun. These conditions are harsh enough to combust most toxic-waste compounds in the water, breaking them down into harmless components.

Professor Hoffmann has employed a device that uses ultrasound—sound waves at frequencies just above the range of human hearing—to create cavitation in polluted water. As water flows between two panels that generate ultrasound at different frequencies, the ultrasonic waves generated by one panel form cavitation bubbles. An instant later, the ultrasound produced by the other panel collapses the bubbles. The intense pressure and heat generated break down the complex toxic compounds into simple, innocuous substances such as carbon dioxide, chloride ions, and hydrogen ions.

"With ultrasound," says Hoffmann, "we can harness frequencies . . . of about 16 kilohertz up to 1 megahertz, and different . . . compounds are destroyed more readily at one frequency versus another . . . applying a particular frequency range, we can destroy a very broad range of chemical compounds."

The device destroys simple toxins in a few minutes and other toxins in several hours. Some compounds must be broken down into intermediate chemicals first and then treated again to destroy them completely. To be sure the waste is totally removed, scientists use sophisticated tracking methods to trace what happens to every single molecule of the toxin.

The ultrasound toxic-waste destroyer treats about 10% of all types of waste, eliminating both organic and inorganic compounds, such as hydrogen cyanide, TNT, and many pesticides. While the device cannot destroy complex mixtures of compounds, such as those found in raw sewage, it does have many advantages over current technologies. Aside from having no harmful environmental side effects, ultrasonic waste destruction is much cheaper and simpler than the process of combustion. By using the destroyer preventively, manufacturers can pretreat their waste products before they dump them in the sewer, thus stopping a problem before it starts.

How does Dr. Hoffmann's ultrasound device benefit society?

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Characteristics of the Covalent Bond

In Figure 6-5 on page 165, the bottom of the valley in the curve represents the balance between attraction and repulsion in a stable covalent bond. At this point, the electrons of each hydrogen atom of the hydrogen molecule are shared between the nuclei. As shown below in Figure 6-7, the molecule's electrons can be pictured as occupying overlapping orbitals, moving about freely in either orbital.

The bonded atoms vibrate a bit, but as long as their potential energy remains close to the minimum, they are covalently bonded to each other. *The distance between two bonded atoms at their minimum potential energy, that is, the average distance between two bonded atoms, is the* **bond length.** The bond length of a hydrogen-hydrogen bond is 75 pm.

In forming a covalent bond, the hydrogen atoms need to release energy as they change from isolated individual atoms to parts of a molecule. The amount of energy released equals the difference between the potential energy at the zero level (separated atoms) and that at the bottom of the valley (bonded atoms) in Figure 6-5. The same amount of energy must be added to separate the bonded atoms. **Bond energy** *is the energy required to break a chemical bond and form neutral isolated atoms.* Scientists usually report bond energies in kilojoules per mole (kJ/mol), which indicates the energy required to break one mole of bonds in isolated molecules. For example, 436 kJ of energy is needed to break the hydrogen-hydrogen bonds in one mole of hydrogen molecules and form two moles of separated hydrogen atoms.

The energy relationships described here for the formation of a hydrogen-hydrogen bond apply generally to all covalent bonds. However, bond lengths and bond energies vary with the types of atoms that have combined. Even the energy of a bond between the same two types of atoms varies somewhat, depending on what other bonds the atoms have formed. These facts should be considered in examining the data in Table 6-1 on page 168. The first three columns in the table list bonds, bond lengths, and bond energies of atoms in specific diatomic molecules. The last three columns give average values of specified bonds in many different compounds.

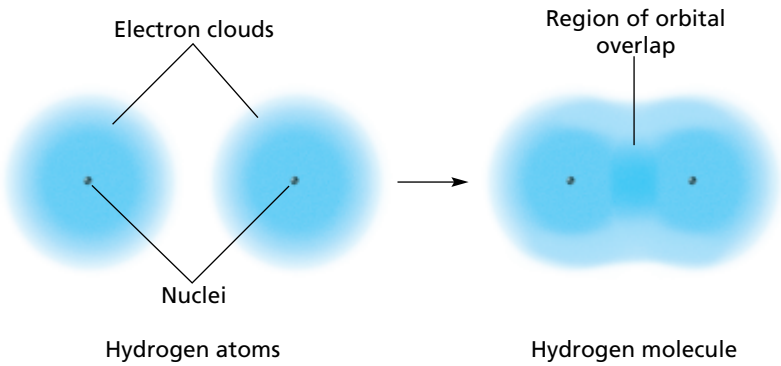

FIGURE 6-7 The orbitals of the hydrogen atoms in a hydrogen molecule overlap, allowing each electron to feel the attraction of both nuclei. The result is an increase in electron density between the nuclei.

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TABLE 6-1 Bond Lengths and Bond Energies for Selected Covalent Bonds

Bond	Bond length (pm)	Bond energy (kJ/mol)	Bond	Bond length (pm)	Bond energy (kJ/mol)
H–H	74	436	C–C	154	346
F–F	141	159	C–N	147	305
Cl–Cl	199	243	C–O	143	358
Br–Br	228	193	C–H	109	418
I–I	267	151	C–Cl	177	327
H–F	92	569	C–Br	194	285
H–Cl	127	432	N–N	145	163
H–Br	141	366	N–H	101	386
H–I	161	299	O–H	96	459

All individual hydrogen atoms contain a single, unpaired electron in a 1*s* atomic orbital. When two hydrogen atoms form a molecule, they share electrons in a covalent bond. As illustrated in Figure 6-8, sharing electrons allows each atom in the hydrogen molecule to experience the effect of the stable electron configuration of helium, $1s^2$. This tendency for atoms to achieve noble-gas configurations through covalent bonding extends beyond the simple case of a hydrogen molecule.

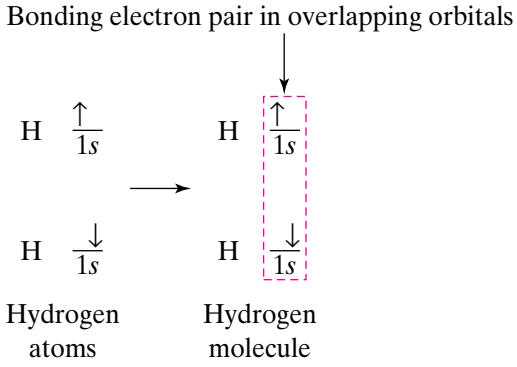

FIGURE 6-8 By sharing electrons in overlapping orbitals, each hydrogen atom in a hydrogen molecule experiences the effect of a stable $1s^2$ configuration.

The Octet Rule

Unlike other atoms, the noble-gas atoms exist independently in nature. They possess a minimum of energy existing on their own because of the special stability of their electron configurations. This stability results from the fact that, with the exception of helium and its two electrons in a completely filled outer shell, the noble-gas atoms' outer *s* and *p* orbitals are completely filled by a total of eight electrons. Other main-group atoms can effectively fill their outermost *s* and *p* orbitals with

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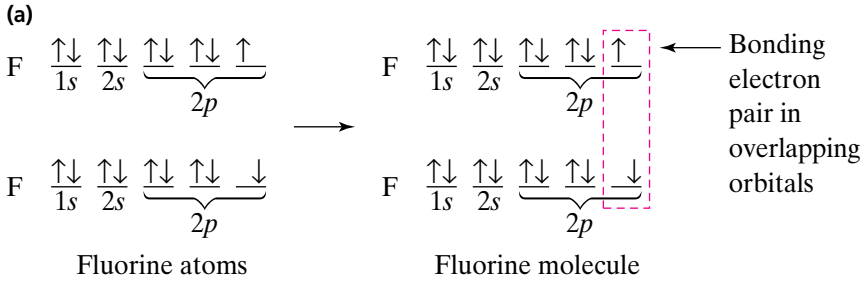
electrons by sharing electrons through covalent bonding. Such bond formation follows the **octet rule:** *Chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has an octet of electrons in its highest occupied energy level.*

Let's examine how the bonding in a fluorine molecule illustrates the octet rule. An independent fluorine atom has seven electrons in its highest energy level ($[He]2s^2 2p^5$). Like hydrogen atoms, fluorine atoms bond covalently with each other to form diatomic molecules, F_2. When two fluorine atoms bond, each atom shares one of its valence electrons with its partner. The shared electron pair effectively fills each atom's outermost energy level with an octet of electrons, as illustrated in Figure 6-9(a). Figure 6-9(b) shows another example of the octet rule, in which the chlorine atom in a molecule of hydrogen chloride, HCl, achieves an outermost octet by sharing an electron pair with an atom of hydrogen.



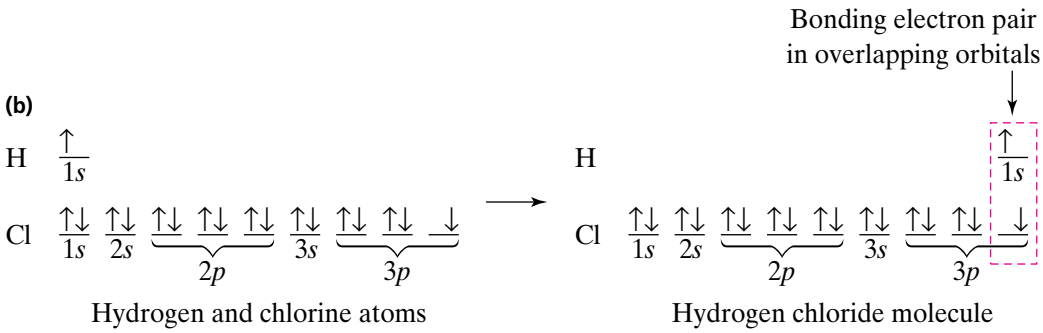


FIGURE 6-9 (a) By sharing valence electrons in overlapping orbitals, each atom in a fluorine molecule feels the effect of neon's stable configuration, $[He]2s^2 2p^6$. (b) In a hydrogen chloride molecule, the hydrogen atom effectively fills its 1*s* orbital with two electrons, while the chlorine atom experiences the stability of an outermost octet of electrons.

Exceptions to the Octet Rule

Most main-group elements tend to form covalent bonds according to the octet rule. However, there are exceptions. As you have seen, hydrogen forms bonds in which it is surrounded by only two electrons. Boron, B, has just three valence electrons ($[He]2s^2 2p^1$). Because electron pairs are shared in covalent bonds, boron tends to form bonds in which it is surrounded by six electrons. In boron trifluoride, BF_3, for example, the boron atom is surrounded by its own three valence electrons plus one from each of the three fluorine atoms bonded to it. Other elements can be surrounded by *more* than eight electrons when they combine with the highly electronegative elements fluorine, oxygen, and chlorine. In these cases of *expanded valence,* bonding involves electrons in *d* orbitals as well as in *s* and *p* orbitals.

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Number of valence electrons	Electron-dot notation	Example
1	$\cdot\mathrm{X}$	$\cdot\mathrm{Na}$
2	$\cdot\mathrm{X}\cdot$	$\cdot\mathrm{Mg}\cdot$
3	$\cdot\dot{\mathrm{X}}\cdot$	$\cdot\dot{\mathrm{B}}\cdot$
4	$\cdot\dot{\mathrm{X}}\cdot$	$\cdot\dot{\mathrm{C}}\cdot$
5	$\cdot\dot{\mathrm{X}}:$	$\cdot\dot{\mathrm{N}}:$
6	$:\dot{\mathrm{X}}:$	$:\dot{\mathrm{O}}:$
7	$:\dot{\mathrm{X}}:$	$:\dot{\mathrm{F}}:$
8	$:\ddot{\mathrm{X}}:$	$:\ddot{\mathrm{Ne}}:$

FIGURE 6-10 To write an element's electron-dot notation, determine the element's number of valence electrons. Then place a corresponding number of dots around the element's symbol, as shown.

Electron-Dot Notation

Covalent bond formation usually involves only the electrons in an atom's outermost energy levels, or the atom's valence electrons. To keep track of these electrons, it is helpful to use electron-dot notation. **Electron-dot notation** *is an electron-configuration notation in which only the valence electrons of an atom of a particular element are shown, indicated by dots placed around the element's symbol.* The inner-shell electrons are not shown. For example, the electron-dot notation for a fluorine atom (electron configuration $[\mathrm{He}]2s^2p^5$) may be written as follows.

$$:\dot{\mathrm{F}}:$$

In general, an element's number of valence electrons can be determined by adding the superscripts of the element's noble-gas notation. In this book, the electron-dot notations for elements with 1–8 valence electrons are written as shown in Figure 6-10.

SAMPLE PROBLEM 6-2

a. Write the electron-dot notation for hydrogen.
b. Write the electron-dot notation for nitrogen.

SOLUTION

a. A hydrogen atom has only one occupied energy level, the $n = 1$ level, which contains a single electron. Therefore, the electron-dot notation for hydrogen is written as follows.

$$\mathrm{H}\cdot$$

b. The group notation for nitrogen's family of elements is ns^2np^3, which indicates that nitrogen has five valence electrons. Therefore, the electron-dot notation for nitrogen is written as follows.

$$\cdot\dot{\mathrm{N}}:$$

Lewis Structures

Electron-dot notation can also be used to represent molecules. For example, a hydrogen molecule, $\mathrm{H_2}$, is represented by combining the notations of two individual hydrogen atoms, as follows.

$$\mathrm{H}:\mathrm{H}$$

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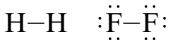
The pair of dots represents the shared electron pair of the hydrogen-hydrogen covalent bond. For a molecule of fluorine, F_2, the electron-dot notations of two fluorine atoms are combined.

Here also the pair of dots between the two symbols represents the shared pair of a covalent bond. In addition, each fluorine atom is surrounded by three pairs of electrons that are not shared in bonds. *An* **unshared pair,** *also called a* **lone pair,** *is a pair of electrons that is not involved in bonding and that belongs exclusively to one atom.*

The pair of dots representing a shared pair of electrons in a covalent bond is often replaced by a long dash. According to this convention, hydrogen and fluorine molecules are represented as follows.



These representations are all **Lewis structures,** *formulas in which atomic symbols represent nuclei and inner-shell electrons, dot-pairs or dashes between two atomic symbols represent electron pairs in covalent bonds, and dots adjacent to only one atomic symbol represent unshared electrons.* It is common to write Lewis structures that show only the electrons that are shared, using dashes to represent the bonds. *A* **structural formula** *indicates the kind, number, arrangement, and bonds but not the unshared pairs of the atoms in a molecule.* For example, F—F and H—Cl are structural formulas.

The Lewis structures (and therefore the structural formulas) for many molecules can be drawn if one knows the composition of the molecule and which atoms are bonded to each other. The following sample problem illustrates the basic steps for writing Lewis structures. The molecule described in this problem contains bonds with single shared electron pairs. A single covalent bond, or a **single bond,** *is a covalent bond produced by the sharing of one pair of electrons between two atoms.*

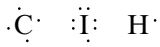
SAMPLE PROBLEM 6-3

Draw the Lewis structure of iodomethane, CH_3I.

SOLUTION

1. *Determine the type and number of atoms in the molecule.*
   The formula shows one carbon atom, one iodine atom, and three hydrogen atoms.

2. *Write the electron-dot notation for each type of atom in the molecule.*
   Carbon is from Group 14 and has four valence electrons. Iodine is from Group 17 and has seven valence electrons. Hydrogen has one valence electron.



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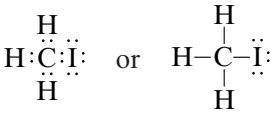
3. *Determine the total number of valence electrons in the atoms to be combined.*

C	$1 \times 4e^-$ =	$4e^-$
I	$1 \times 7e^-$ =	$7e^-$
H	$3 \times 1e^-$ =	$3e^-$
		$14e^-$

4. *Arrange the atoms to form a skeleton structure for the molecule. If carbon is present, it is the central atom. Otherwise, the least-electronegative atom is central (except for hydrogen, which is never central). Then connect the atoms by electron-pair bonds.*

5. *Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by eight electrons.*

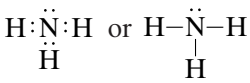


6. *Count the electrons in the structure to be sure that the number of valence electrons used equals the number available. Be sure the central atom and other atoms besides hydrogen have an octet.*
There are eight electrons in the four covalent bonds and six electrons in the three unshared pairs, giving the correct total of 14 valence electrons.

PRACTICE

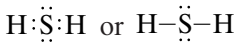
1. Draw the Lewis structure of ammonia, NH_3.

Answer



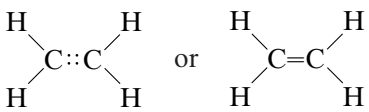
2. Draw the Lewis structure for hydrogen sulfide, H_2S.

Answer



Multiple Covalent Bonds

Atoms of some elements, especially carbon, nitrogen, and oxygen, can share more than one electron pair. A double covalent bond, or simply a **double bond,** *is a covalent bond produced by the sharing of two pairs of electrons between two atoms.* A double bond is shown either by two side-by-side pairs of dots or by two parallel dashes. All four electrons in a double bond "belong" to both atoms. In ethene, C_2H_4, for example, two electron pairs are simultaneously shared by two carbon atoms.



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A triple covalent bond, or simply a **triple bond,** *is a covalent bond produced by the sharing of three pairs of electrons between two atoms.* For example, elemental nitrogen, N_2, like hydrogen and the halogens, normally exists as diatomic molecules. In this case, however, each nitrogen atom, which has five valence electrons, acquires three electrons to complete an octet by sharing three pairs of electrons with its partner. This is illustrated in the Lewis structure and the formula structure for N_2, as shown below.

$$:N\vdots\vdots N: \quad \text{or} \quad N\equiv N$$

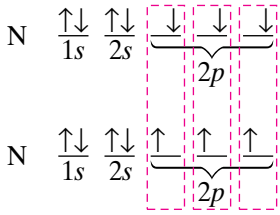
Figure 6-11 represents nitrogen's triple bond through orbital notation. Like the single bonds in hydrogen and halogen molecules, the triple bond in nitrogen molecules is nonpolar.

Carbon forms a number of compounds containing triple bonds. For example, the compound ethyne, C_2H_2, contains a carbon-carbon triple bond.

$$H:C\vdots\vdots C:H \quad \text{or} \quad H-C\equiv C-H$$

Double and triple bonds are referred to as **multiple bonds,** or multiple covalent bonds. Double bonds in general have higher bond energies and are shorter than single bonds. Triple bonds are even stronger and shorter. Table 6-2 compares average bond lengths and bond energies for some single, double, and triple bonds.

In writing Lewis structures for molecules that contain carbon, nitrogen, or oxygen, one must remember that multiple bonds between pairs of these atoms are possible. (A hydrogen atom, on the other hand, has only one electron and therefore always forms a single covalent bond.) The need for a multiple bond becomes obvious if there are not enough valence electrons to complete octets by adding unshared pairs. Sample Problem 6-4 on page 174 illustrates how to deal with this situation.



Nitrogen molecule

FIGURE 6-11 In a molecule of nitrogen, N_2, each nitrogen atom is surrounded by six shared electrons plus one unshared pair of electrons. Thus, each nitrogen atom follows the octet rule in forming a triple covalent bond.

TABLE 6-2 *Bond Lengths and Bond Energies for Single and Multiple Covalent Bonds*

Bond	Bond length (pm)	Bond energy (kJ/mol)	Bond	Bond length (pm)	Bond energy (kJ/mol)
C−C	154	346	C−O	143	358
C=C	134	612	C=O	120	732
C≡C	120	835	C≡O	113	1072
C−N	147	305	N−N	145	163
C=N	132	615	N=N	125	418
C≡N	116	887	N≡N	110	945

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SAMPLE PROBLEM 6-4

Draw the Lewis structure for methanal, CH_2O, which is also known as formaldehyde.

SOLUTION

1. *Determine the number of atoms of each element present in the molecule.*
The formula shows one carbon atom, two hydrogen atoms, and one oxygen atom.

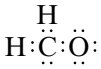
2. *Write the electron-dot notation for each type of atom.*
Carbon from Group 14 has four valence electrons. Oxygen, which is in Group 16, has six valence electrons. Hydrogen has only one electron.

3. *Determine the total number of valence electrons in the atoms to be combined.*

C	**$1 \times 4e^-$**	**$= 4e^-$**
O	**$1 \times 6e^-$**	**$= 6e^-$**
2H	**$2 \times 1e^-$**	**$= 2e^-$**
		$12e^-$

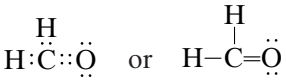
4. *Arrange the atoms to form a skeleton structure for the molecule, and connect the atoms by electron-pair bonds.*

5. *Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by eight electrons.*



6a. *Count the electrons in the Lewis structure to be sure that the number of valence electrons used equals the number available.*
The structure above has six electrons in covalent bonds and eight electrons in four lone pairs, for a total of 14 electrons. The structure has two valence electrons too many.

6b. *If too many electrons have been used, subtract one or more lone pairs until the total number of valence electrons is correct. Then move one or more lone electron pairs to existing bonds between non-hydrogen atoms until the outer shells of all atoms are completely filled.*
Subtract the lone pair of electrons from the carbon atom. Then move one lone pair of electrons from the oxygen to the bond between carbon and oxygen to form a double bond.

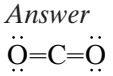


There are eight electrons in covalent bonds and four electrons in lone pairs, for a total of 12 valence electrons.

PRACTICE

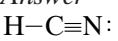
1. Draw the Lewis structure for carbon dioxide, CO_2.

Answer



2. Draw the Lewis structure for hydrogen cyanide, which contains one hydrogen atom, one carbon atom, and one nitrogen atom.

Answer



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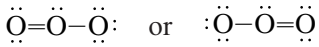
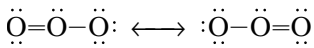
Resonance Structures

Some molecules and ions cannot be represented adequately by a single Lewis structure. One such molecule is ozone, O_3, which can be represented by either of the following Lewis structures.



Notice that each structure indicates that the ozone molecule has two types of O—O bonds, one single and one double. Chemists once speculated that ozone split its time existing as one of these two structures, constantly alternating, or "resonating," from one to the other. Experiments, however, revealed that the oxygen-oxygen bonds in ozone are identical. Therefore, scientists now say that ozone has a single structure that is the average of these two structures. Together the structures are referred to as *resonance structures* or *resonance hybrids*. **Resonance** *refers to bonding in molecules or ions that cannot be correctly represented by a single Lewis structure.* To indicate resonance, a double-headed arrow is placed between a molecule's resonance structures.



Covalent-Network Bonding

All the covalent compounds that you have read about to this point are molecular. They consist of many identical molecules bound together by forces acting between the molecules. (You will read more about intermolecular forces in Section 6-5.) There are many covalently bonded compounds that do not contain individual molecules, but instead can be pictured as continuous, three-dimensional networks of bonded atoms. You will read more about covalently bonded networks in Chapter 11.

SECTION REVIEW

1. Define the following:
   a. bond length b. bond energy
2. State the octet rule.
3. How many pairs of electrons are shared in the following types of covalent bonds?
   a. a single bond
   b. a double bond
   c. a triple bond
4. Draw the Lewis structures for the following molecules:
   a. IBr
   b. CH_3Br
   c. C_2HCl
   d. $SiCl_4$
   e. F_2O

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SECTION 6-3

Objectives

- Compare and contrast a chemical formula for a molecular compound with one for an ionic compound.
- Discuss the arrangements of ions in crystals.
- Define *lattice energy* and explain its significance.
- List and compare the distinctive properties of ionic and molecular compounds.
- Write the Lewis structure for a polyatomic ion given the identity of the atoms combined and other appropriate information.

Ionic Bonding and Ionic Compounds

Most of the rocks and minerals that make up Earth's crust consist of positive and negative ions held together by ionic bonding. A familiar example of an ionically bonded compound is sodium chloride, or common table salt, which is found in nature as rock salt. A sodium ion, Na^+, has a charge of 1+. A chloride ion, Cl^-, has a charge of 1–. In sodium chloride, these ions combine in a one-to-one ratio—Na^+Cl^-—so that each positive charge is balanced by a negative charge. Because chemists are aware of this balance of charge, the chemical formula for sodium chloride is usually written simply as NaCl.

An **ionic compound** *is composed of positive and negative ions that are combined so that the numbers of positive and negative charges are equal.* Most ionic compounds exist as crystalline solids (see Figure 6-12). A crystal of any ionic compound is a three-dimensional network of positive and negative ions mutually attracted to one another. As a result, in contrast to a molecular compound, an ionic compound is not composed of independent, neutral units that can be isolated and examined. The chemical formula of an ionic compound merely represents the simplest ratio of the compound's combined ions that gives electrical neutrality.

The chemical formula of an ionic compound shows the ratio of the ions present in a sample of any size. *A* **formula unit** *is the simplest collection of atoms from which an ionic compound's formula can be established.* For example, one formula unit of sodium chloride, NaCl, is one sodium cation plus one chloride anion. (In naming anions, the *-ine* ending of the element's name is replaced with *-ide*. You'll read more about naming compounds in Chapter 7.)

The ratio of ions in a formula unit depends on the charges of the ions combined. For example, to achieve electrical neutrality in the ionic compound calcium fluoride, two fluoride anions, F^-, each with a charge of 1–, must balance the 2+ charge of each calcium cation, Ca^{2+}. Therefore, the formula of calcium fluoride is CaF_2.

FIGURE 6-12 Like most ionic compounds, sodium chloride is a crystalline solid.

Formation of Ionic Compounds

Electron-dot notation can be used to demonstrate the changes that take place in ionic bonding. Ionic compounds do not ordinarily form by the combination of isolated ions, but consider for a moment a sodium

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atom and a chlorine atom approaching each other. The two atoms are neutral and have one and seven valence electrons, respectively.

$Na\cdot$ $\quad$ $:\ddot{\underset{\cdot}{Cl}}:$

Sodium atom $\quad$ Chlorine atom

We have already seen that atoms of sodium and the other alkali metals readily lose one electron to form cations. And we have seen that atoms of chlorine and the other halogens readily gain one electron to form anions. The combination of sodium and chlorine atoms to produce one formula unit of sodium chloride can thus be represented as follows.

$$Na\cdot + :\ddot{\underset{\cdot}{Cl}}: \longrightarrow Na^+ + :\ddot{Cl}:^-$$

Sodium atom $\quad$ Chlorine atom $\quad$ Sodium cation $\quad$ Chloride anion

The transfer of an electron from the sodium atom to the chlorine atom transforms each atom into an ion with a noble-gas configuration. In the combination of calcium with fluorine, two fluorine atoms are needed to accept the two valence electrons given up by one calcium atom.

$$\cdot Ca\cdot + :\ddot{\underset{\cdot}{F}}: + :\ddot{\underset{\cdot}{F}}: \longrightarrow Ca^{2+} + :\ddot{F}:^- + :\ddot{F}:^-$$

Calcium atom $\quad$ Fluorine atoms $\quad$ Calcium cation $\quad$ Fluoride anions

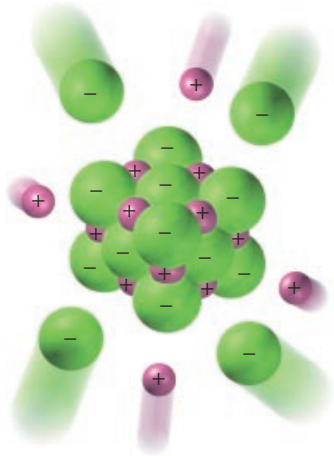

FIGURE 6-13 The ions in an ionic compound lower their potential energy by forming an orderly, three-dimensional array in which the positive and negative charges are balanced. The electrical forces of attraction between oppositely charged ions extend over long distances, causing a large decrease in potential energy.

Characteristics of Ionic Bonding

Recall that nature favors arrangements in which potential energy is minimized. In an ionic crystal, ions minimize their potential energy by combining in an orderly arrangement known as a *crystal lattice* (see Figure 6-13). The attractive forces at work within an ionic crystal include those between oppositely charged ions and those between the nuclei and electrons of adjacent ions. The repulsive forces include those between like-charged ions and those between electrons of adjacent ions. The distances between ions and their arrangement in a crystal represent a balance among all these forces. Sodium chloride's crystal structure is shown in Figure 6-14 below.

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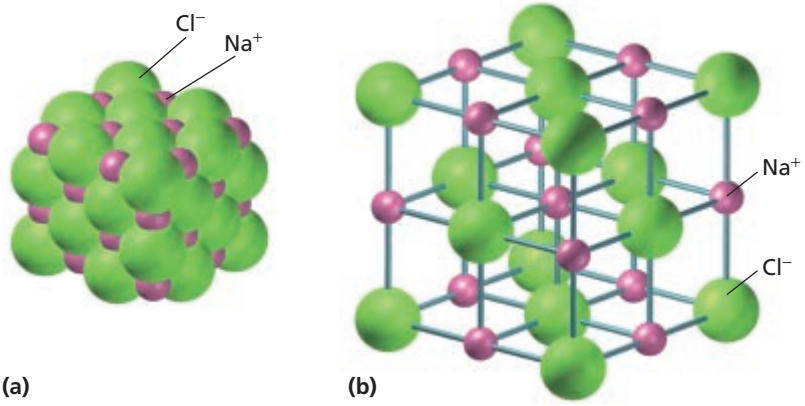

FIGURE 6-14 Two models of the crystal structure of sodium chloride are shown. (a) To illustrate the ions' actual arrangement, the sodium and chloride ions are shown with their electron clouds just touching. (b) In an expanded view, the distances between ions have been exaggerated in order to clarify the positioning of the ions in the structure.

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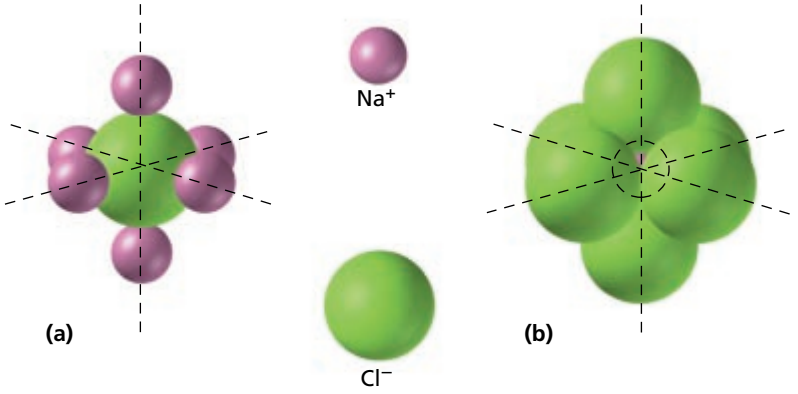

FIGURE 6-15 The figure shows the ions that most closely surround a chloride anion and a sodium cation within the crystal structure of NaCl. The structure is composed such that (a) six Na^+ ions surround each Cl^- ion. At the same time, (b) six Cl^- ions surround each Na^+ ion (which cannot be seen but whose location is indicated by the dashed outline).

Figure 6-15 shows the crystal structure of sodium chloride in greater detail. Within the arrangement, each sodium cation is surrounded by six chloride anions. At the same time, each chloride anion is surrounded by six sodium cations. Attraction between the adjacent oppositely charged ions is much stronger than repulsion by other ions of the same charge, which are farther away.

The three-dimensional arrangements of ions and the strengths of attraction between them vary with the sizes and charges of the ions and the numbers of ions of different charges. For example, in calcium fluoride, there are two anions for each cation. Each calcium cation is surrounded by eight fluoride anions. At the same time, each fluoride ion is surrounded by four calcium cations, as shown in Figure 6-16.

To compare bond strengths in ionic compounds, chemists compare the amounts of energy released when separated ions in a gas come together to form a crystalline solid. **Lattice energy** *is the energy released when one mole of an ionic crystalline compound is formed from gaseous ions.* Lattice energy values for a few common ionic compounds are shown in Table 6-3. The negative energy values indicate that energy is *released* when the crystals are formed.

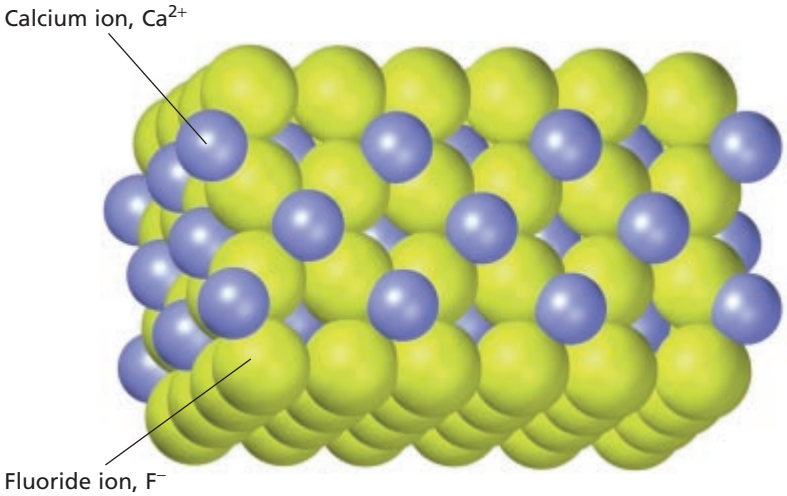

FIGURE 6-16 In the crystal structure of calcium fluoride, CaF_2, each calcium cation is surrounded by eight fluoride anions and each fluoride ion is surrounded by four calcium cations. This is the closest possible packing of the ions in which the positive and negative charges are balanced.

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A Comparison of Ionic and Molecular Compounds

The force that holds ions together in ionic compounds is a very strong overall attraction between positive and negative charges. In a molecular compound, the covalent bonds of the atoms making up each molecule are also strong. But the forces of attraction *between* molecules are much weaker than the forces of ionic bonding. This difference in the strength of attraction between the basic units of molecular and ionic compounds gives rise to different properties in the two types of compounds.

The melting point, boiling point, and hardness of a compound depend on how strongly its basic units are attracted to each other. Because the forces of attraction between individual molecules are not very strong, many molecular compounds melt at low temperatures. In fact, many molecular compounds are already completely gaseous at room temperature. In contrast, the ions in ionic compounds are held together by strong attractive forces, so ionic compounds generally have higher melting and boiling points than do molecular compounds. Further, they do not vaporize at room temperature as many molecular compounds do.

Ionic compounds are hard but brittle. Why? In an ionic crystal, even a slight shift of one row of ions relative to another causes a large buildup of repulsive forces, as shown in Figure 6-17. These forces make it difficult for one layer to move relative to another, causing ionic compounds to be hard. If one layer is moved, however, the repulsive forces make the layers part completely, causing ionic compounds to be brittle.

In the solid state, the ions cannot move, so the compounds are not electrical conductors. In the molten state, ionic compounds are electrical conductors because the ions can move freely to carry electrical current. Many ionic compounds can dissolve in water. When they dissolve, their ions separate from each other and become surrounded by water molecules. These ions are free to move through the solution, so such solutions are electrical conductors. Other ionic compounds do not dissolve in water, however, because the attraction of the water molecules cannot overcome the attractions between the ions.

TABLE 6-3 *Lattice Energies of Some Common Ionic Compounds*

Compound	Lattice energy (kJ/mol)
NaCl	–787.5
NaBr	–751.4
CaF_2	–2634.7
CaO	–3385
LiCl	–861.3
LiF	–1032
MgO	–3760
KCl	–715

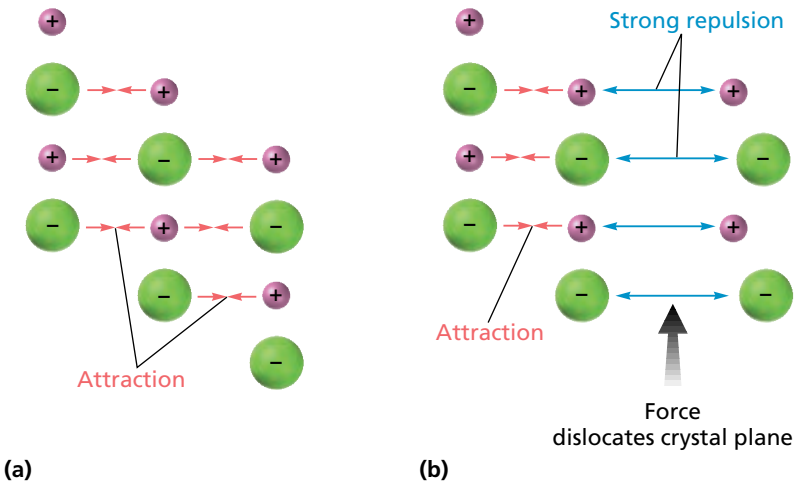

FIGURE 6-17 (a) The attraction between positive and negative ions in a crystalline ionic compound causes layers of ions to resist motion. (b) When struck with sufficient force, the layers shift so that ions of the same charge approach each other, causing repulsion. As a result, the crystal shatters along the planes.

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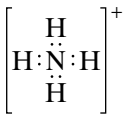
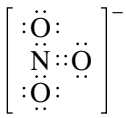
Polyatomic Ions

Certain atoms bond covalently with each other to form a group of atoms that has both molecular and ionic characteristics. *A charged group of covalently bonded atoms is known as a* **polyatomic ion.** Polyatomic ions combine with ions of opposite charge to form ionic compounds. The charge of a polyatomic ion results from an excess of electrons (negative charge) or a shortage of electrons (positive charge). For example, an ammonium ion, a common positively charged polyatomic ion, contains one nitrogen atom and four hydrogen atoms and has a single positive charge. Its formula is NH_4^+, sometimes written as $[NH_4]^+$ to show that the group of atoms *as a whole* has a charge of 1+. The seven protons in the nitrogen atom plus the four protons in the four hydrogen atoms give the ammonium ion a total positive charge of 11+. An independent nitrogen atom has seven electrons, and four independent hydrogen atoms have a total of four electrons. When these atoms combine to form an ammonium ion, one of their electrons is lost, giving the polyatomic ion a total negative charge of 10–.

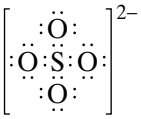
Lewis structures for the ammonium ion and some common negative polyatomic ions—the nitrate, sulfate, and phosphate ions—are shown below. To find the Lewis structure for a polyatomic ion, follow the steps of Sample Problem 6-4 on page 174, with the following exception. If the ion is negatively charged, add to the total number of valence electrons a number of e^- corresponding to the ion's negative charge. If the ion is positively charged, subtract from the total number of valence electrons a number of e^- corresponding to the ion's positive charge.



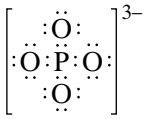
Ammonium ion



Nitrate ion



Sulfate ion



Phosphate ion

SECTION REVIEW

1. Give two examples of an ionic compound.
2. Use electron-dot notation to demonstrate the formation of ionic compounds involving the following:
   a. Li and Cl
   b. Ca and I
3. Distinguish between ionic and molecular compounds in terms of the basic units that each is composed of.
4. Compound B has lower melting and boiling points than compound A. At the same temperature, compound B vaporizes faster and to a greater extent than compound A. If one of these compounds is ionic and the other is molecular, which would you expect to be molecular? ionic? Explain the reasoning behind your choices.

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Metallic Bonding

SECTION 6-4

Objectives

- Describe the electron-sea model of metallic bonding, and explain why metals are good electrical conductors.
- Explain why metal surfaces are shiny.
- Explain why metals are malleable and ductile but ionic-crystalline compounds are not.

Chemical bonding is different in metals than it is in ionic, molecular, or covalent-network compounds. This difference is reflected in the unique properties of metals. They are excellent electrical conductors in the solid state—much better conductors than even molten ionic compounds. This property is due to the highly mobile valence electrons of the atoms that make up a metal. Such mobility is not possible in molecular compounds, in which valence electrons are localized in electron-pair bonds between neutral atoms. Nor is it possible in solid ionic compounds, in which electrons are bound to individual ions that are held in place in crystal structures.

The Metallic-Bond Model

The highest energy levels of most metal atoms are occupied by very few electrons. In *s*-block metals, for example, one or two valence electrons occupy the outermost orbital, whereas all three outermost *p* orbitals, which can hold a total of six electrons, are vacant. In addition to completely vacant outer *p* orbitals, *d*-block metals also possess many vacant *d* orbitals in the energy level just below their highest energy level.

Within a metal, the vacant orbitals in the atoms' outer energy levels overlap. This overlapping of orbitals allows the outer electrons of the atoms to roam freely throughout the entire metal. The electrons are *delocalized,* which means that they do not belong to any one atom but move freely about the metal's network of empty atomic orbitals. These mobile electrons form a *sea of electrons* around the metal atoms, which are packed together in a crystal lattice (see Figure 6-18). *The chemical bonding that results from the attraction between metal atoms and the surrounding sea of electrons is called* **metallic bonding.**

Metallic Properties

The freedom of electrons to move in a network of metal atoms accounts for the high electrical and thermal conductivity characteristic of all metals. In addition, because they contain many orbitals separated by extremely small energy differences, metals can absorb a wide range of light frequencies. This absorption of light results in the excitation of the metal atoms' electrons to higher energy levels. The electrons immediately fall back down to lower levels, emitting energy in the form of light. This de-excitation is responsible for the shiny appearance of metal surfaces.

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FIGURE 6-18 The model shows a portion of the crystal structure of solid sodium. The atoms are arranged so that each sodium atom is surrounded by eight other sodium atoms. The atoms are relatively fixed in position, while the electrons are free to move throughout the crystal, forming an electron sea.

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FIGURE 6-19 Unlike ionic crystalline compounds, most metals are malleable. This property allows iron, for example, to be shaped into useful tools.

Most metals are also easy to form into desired shapes. Two important properties related to this characteristic are malleability and ductility. **Malleability** *is the ability of a substance to be hammered or beaten into thin sheets*. **Ductility** *is the ability of a substance to be drawn, pulled, or extruded through a small opening to produce a wire.* The malleability and ductility of metals are possible because metallic bonding is the same in all directions throughout the solid. One plane of atoms in a metal can slide past another without encountering any resistance or breaking any bonds. By contrast, recall from Section 6-3 that shifting the layers of an ionic crystal causes the bonds to break and the crystal to shatter.

Metallic Bond Strength

Metallic bond strength varies with the nuclear charge of the metal atoms and the number of electrons in the metal's electron sea. Both of these factors are reflected in a metal's *heat of vaporization*. When a metal is vaporized, the bonded atoms in the normal (usually solid) state are converted to individual metal atoms in the gaseous state. The amount of heat required to vaporize the metal is a measure of the strength of the bonds that hold the metal together. Some heats of vaporization for metals are given in Table 6-4.

TABLE 6-4 ***Heats of Vaporization of Some Metals (kJ/mol)***

Period	Element		
Second	Li 147	Be 297	
Third	Na 97	Mg 128	Al 294
Fourth	K 77	Ca 155	Sc 333
Fifth	Rb 76	Sr 137	Y 365
Sixth	Cs 64	Ba 140	La 402

SECTION REVIEW

1. Describe the electron-sea model of metallic bonding.
2. What is the relationship between metallic bond strength and heat of vaporization?
3. Explain why most metals are malleable and ductile but ionic crystals are not.

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Molecular Geometry

SECTION 6-5

Objectives

- Explain VSEPR theory.
- Predict the shapes of molecules or polyatomic ions using VSEPR theory.
- Explain how the shapes of molecules are accounted for by hybridization theory.
- Describe dipole-dipole forces, hydrogen bonding, induced dipoles, and London dispersion forces.
- Explain what determines molecular polarity.

The properties of molecules depend not only on the bonding of atoms but also on molecular geometry—the three-dimensional arrangement of a molecule's atoms in space. The polarity of each bond, along with the geometry of the molecule, determines **molecular polarity,** *or the uneven distribution of molecular charge*. As you will read, molecular polarity strongly influences the forces that act *between* molecules in liquids and solids.

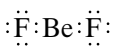
A chemical formula reveals little information about a molecule's geometry. After performing many tests designed to reveal the shapes of various molecules, chemists developed two different, equally successful theories to explain certain aspects of their findings. One theory accounts for molecular bond angles. The other is used to describe the orbitals that contain the valence electrons of a molecule's atoms.

VSEPR Theory

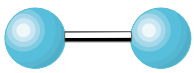
As shown in Figure 6-20, diatomic molecules, like those of hydrogen, H_2, and hydrogen chloride, HCl, must be linear because they consist of only two atoms. To predict the geometries of more-complicated molecules, one must consider the locations of all electron pairs surrounding the bonded atoms. This is the basis of VSEPR theory.

The abbreviation VSEPR stands for "valence-shell, electron-pair repulsion," referring to the repulsion between pairs of valence electrons of the atoms in a molecule. **VSEPR theory** *states that repulsion between the sets of valence-level electrons surrounding an atom causes these sets to be oriented as far apart as possible.* How does the assumption that electrons in molecules repel each other account for molecular shapes? For now let us consider only molecules with no unshared valence electron pairs on the central atom.

Let's examine the simple molecule BeF_2. Recall that beryllium does not follow the octet rule. The beryllium atom forms a covalent bond with each fluorine atom. It is surrounded by only the two electron pairs that it shares with the fluorine atoms.



According to VSEPR, the shared pairs are oriented as far away from each other as possible. As shown in Figure 6-21(a) on page 184, the distance between electron pairs is maximized if the bonds to fluorine are



(a) Hydrogen, H_2

(b) Hydrogen chloride, HCl

FIGURE 6-20 Ball-and-stick models illustrate the linearity of diatomic molecules. (a) A hydrogen molecule is represented by two identical balls (the hydrogen atoms) joined by a solid bar (the covalent bond). (b) A hydrogen chloride molecule is composed of dissimilar atoms, but it is still linear.

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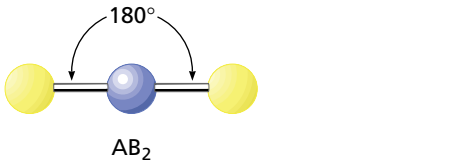
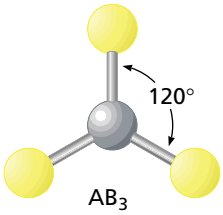


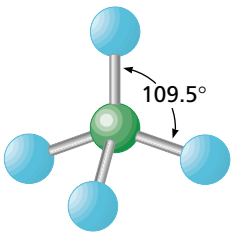
AB_2

(a) Beryllium fluoride, BeF_2



AB_3

(b) Boron trifluoride, BF_3



AB_4

(c) Methane, CH_4

FIGURE 6-21 Ball-and-stick models show the shapes of (a) AB_2, (b) AB_3, and (c) AB_4 molecules according to VSEPR.

on opposite sides of the beryllium atom, 180° apart. Thus, all three atoms lie on a straight line. The molecule is linear.

If we represent the central atom in a molecule by the letter *A* and we represent the atoms bonded to the central atom by the letter *B*, then according to VSEPR, BeF_2 is an example of an AB_2 molecule, which is linear. Can you determine what an AB_3 molecule looks like? The three A—B bonds stay farthest apart by pointing to the corners of an equilateral triangle, giving 120° angles between the bonds. This trigonal-planar geometry is shown in Figure 6-21(b) for the AB_3 molecule boron trifluoride, BF_3.

Unlike AB_2 and AB_3 molecules, the central atoms in AB_4 molecules follow the octet rule by sharing four electron pairs with B atoms. The distance between electron pairs is maximized if each A—B bond points to one of four corners of a tetrahedron. This geometry is shown in Figure 6-21(c) for the AB_4 molecule methane, CH_4. The same figure shows that in a tetrahedral molecule, each of the bond angles formed by the A atom and any two of the B atoms is equal to 109.5°.

The shapes of various molecules are summarized in Table 6-5 on page 186. B can represent a single type of atom, a group of identical atoms, or a group of different atoms on the same molecule. The shape of the molecule will still be based on the forms given in the table. However, different sizes of B groups distort the bond angles, making some bond angles larger or smaller than those given in the table.

SAMPLE PROBLEM 6-5

Use VSEPR theory to predict the molecular geometry of aluminum trichloride, $AlCl_3$.

SOLUTION

First write the Lewis structure for $AlCl_3$. Aluminum is in Group 13 and has three valence electrons.

$$\cdot\dot{\mathrm{Al}}\cdot$$

Chlorine is in Group 17 and has seven valence electrons.

$$:\ddot{\mathrm{Cl}}:$$

The total number of available valence electrons is therefore $24e^-$ ($3e^-$ from aluminum and $21e^-$ from chlorine). The following Lewis structure uses all $24e^-$.

$$\begin{array}{c} :\ddot{\mathrm{Cl}}: \\ :\ddot{\mathrm{Cl}}:\dot{\mathrm{Al}}:\ddot{\mathrm{Cl}}: \end{array}$$

This molecule is an exception to the octet rule because in this case Al forms only three bonds. Aluminum trichloride is an AB_3 type of molecule. Therefore, according to VSEPR theory, it should have trigonal-planar geometry.

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PRACTICE

1. Use VSEPR theory to predict the molecular geometry of the following molecules:
   a. HI c. $AlBr_3$
   b. CBr_4 d. CH_2Cl_2

Answer
a. linear c. trigonal-planar
b. tetrahedral d. tetrahedral

VSEPR and Unshared Electron Pairs

Ammonia, NH_3, and water, H_2O, are examples of molecules in which the central atom has both shared and unshared electron pairs (see Table 6-5 for their Lewis structures). How does VSEPR theory account for the geometries of these molecules?

The Lewis structure of ammonia shows that in addition to the three electron pairs it shares with the three hydrogen atoms, the central nitrogen atom has one unshared pair of electrons.

VSEPR theory postulates that the lone pair occupies space around the nitrogen atom just as the bonding pairs do. Thus, as in an AB_4 molecule, the electron pairs maximize their separation by assuming the four corners of a tetrahedron. Lone pairs do occupy space, but our description of the observed shape of a molecule refers to the *positions of atoms only*. Consequently, as shown in Figure 6-22(a), the molecular geometry of an ammonia molecule is that of a pyramid with a triangular base. The general VSEPR formula for molecules such as ammonia is AB_3E, where E represents the unshared electron pair.

A water molecule has two unshared electron pairs. It is an AB_2E_2 molecule. Here, the oxygen atom is at the center of a tetrahedron, with two corners occupied by hydrogen atoms and two by the unshared pairs (Figure 6-22(b)). Again, VSEPR theory states that the lone pairs occupy space around the central atom but that the actual shape of the molecule is determined by the positions of the atoms only. In the case of water, this results in a "bent," or angular, molecule.

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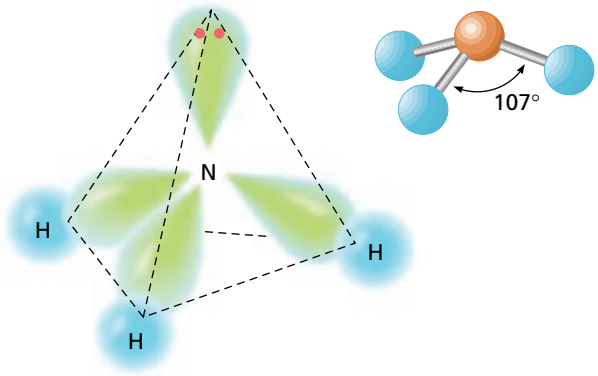
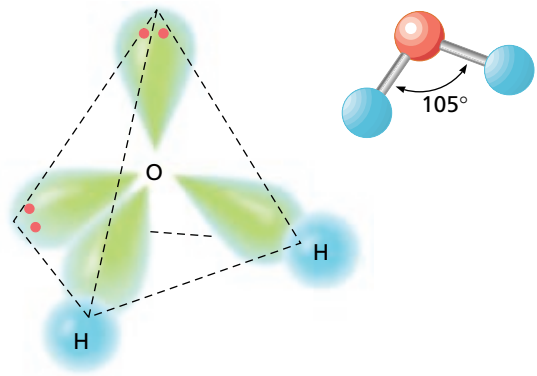
FIGURE 6-22 The locations of bonds and unshared electrons are shown for molecules of (a) ammonia and (b) water. Although unshared electrons occupy space around the central atoms, the shapes of the molecules depend only on the position of the molecules' atoms, as clearly shown by the ball-and-stick models.



(a) Ammonia, NH_3



(b) Water, H_2O

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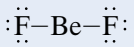
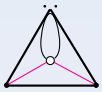
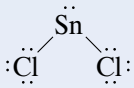
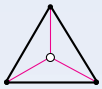
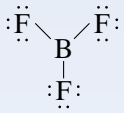
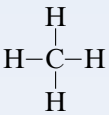
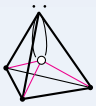
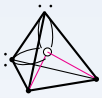
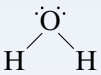
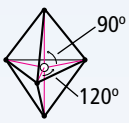
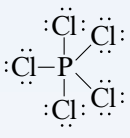
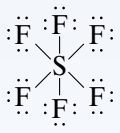
In Figure 6-22(b), note that the bond angles in ammonia and water are somewhat less than the 109.5° bond angles of a perfectly tetrahedral molecule. These angles are smaller because the unshared electron pairs repel electrons more strongly than do bonding electron pairs.

Table 6-5 also includes an example of an AB_2E type molecule. This type of molecule results when a central atom forms two bonds and retains one unshared electron pair.

Finally, in VSEPR theory, double and triple bonds are treated in the same way as single bonds. And polyatomic ions are treated similarly to molecules. (Remember to consider *all* of the electron pairs present in any ion or molecule.) Thus, Lewis structures and Table 6-5 can be used together to predict the shapes of polyatomic ions as well as molecules with double or triple bonds.

TABLE 6-5 *VSEPR and Molecular Geometry*

	Molecular shape	Atoms bonded to central atom	Lone pairs of electrons	Type of molecule	Formula example	Lewis structure
Linear		2	0	AB_2	BeF_2	
Bent or angular		2	1	AB_2E	$SnCl_2$	
Trigonal-planar		3	0	AB_3	BF_3	
Tetrahedral		4	0	AB_4	CH_4	
Trigonal-pyramidal		3	1	AB_3E	NH_3	
Bent or angular		2	2	AB_2E_2	H_2O	
Trigonal-bipyramidal		5	0	AB_5	PCl_5	
Octahedral		6	0	AB_6	SF_6	

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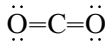
SAMPLE PROBLEM 6-6

a. Use VSEPR theory to predict the shape of a molecule of carbon dioxide, CO_2.
b. Use VSEPR theory to predict the shape of a chlorate ion, ClO_3^-.

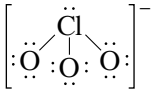
SOLUTION

a. The Lewis structure of carbon dioxide shows two carbon-oxygen double bonds and no unshared electron pairs on the carbon atom. To simplify the molecule's Lewis structure, we represent the covalent bonds with lines instead of dots.



This is an AB_2 molecule, which is linear.

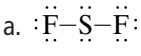
b. The Lewis structure of a chlorate ion shows three oxygen atoms and an unshared pair of electrons surrounding a central chlorine atom. Again, lines are used to represent the covalent bonds.

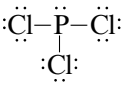


The chlorate ion is an AB_3E type. It has trigonal-pyramidal geometry, with the three oxygen atoms at the base of the pyramid and the chlorine atom at the top.

PRACTICE

1. Use VSEPR theory to predict the molecular geometries of the molecules whose Lewis structures are given below.

a. 

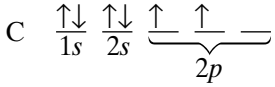
b. 

Answer
a. bent or angular
b. trigonal-pyramidal

Hybridization

VSEPR theory is useful for explaining the shapes of molecules. However, it does not reveal the relationship between a molecule's geometry and the orbitals occupied by its bonding electrons. To explain how the orbitals of an atom become rearranged when the atom forms covalent bonds, a different model is used. This model is called **hybridization,** *which is the mixing of two or more atomic orbitals of similar energies on the same atom to produce new orbitals of equal energies.*

Methane, CH_4, provides a good example of how hybridization is used to explain the geometry of molecular orbitals. The orbital notation for a carbon atom shows that it has four valence electrons, two in the 2*s* orbital and two in 2*p* orbitals.



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We know from experiments that a methane molecule has tetrahedral geometry. How does carbon form four equivalent, tetrahedrally arranged covalent bonds by orbital overlap with four other atoms?

Two of carbon's valence electrons occupy the 2*s* orbital, and two occupy the 2*p* orbitals. Recall that the 2*s* orbital and the 2*p* orbitals have different shapes. To achieve four equivalent bonds, carbon's *2s* and three *2p* orbitals *hybridize* to form four new, identical orbitals called sp^3 orbitals. The superscript 3 indicates that three *p* orbitals were included in the hybridization; the superscript 1 on the *s* is understood. The sp^3 orbitals all have the same energy, which is greater than that of the 2*s* orbital but less than that of the 2*p* orbitals, as shown in Figure 6-23.

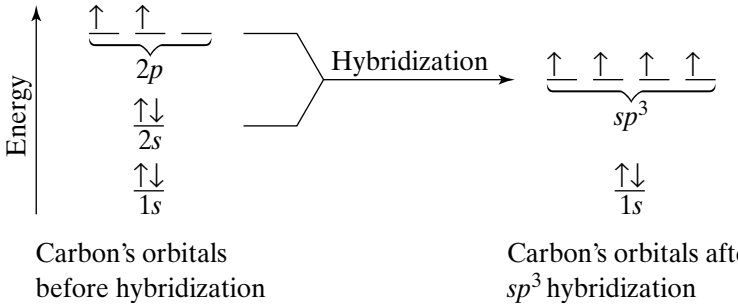
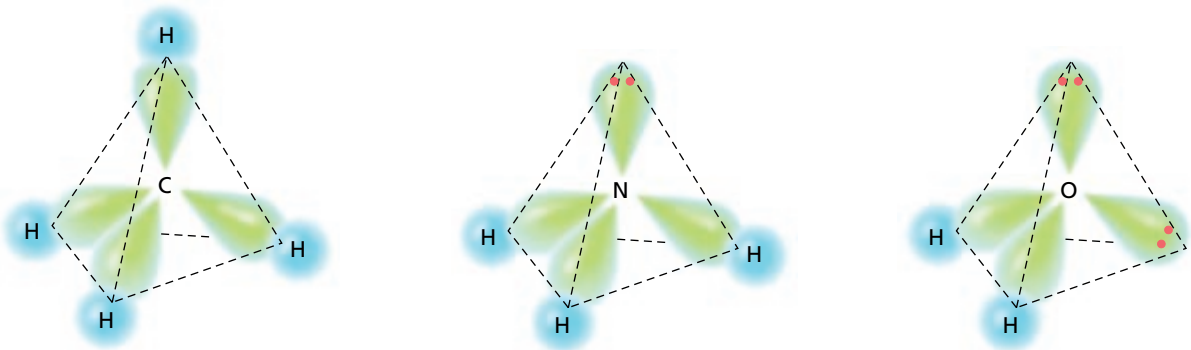


FIGURE 6-23 The sp^3 hybridization of carbon's outer orbitals combines one *s* and three *p* orbitals to form four sp^3 hybrid orbitals. Whenever hybridization occurs, the resulting hybrid orbitals are at an energy level between the levels of the orbitals that have combined.

Hybrid orbitals *are orbitals of equal energy produced by the combination of two or more orbitals on the same atom.* The number of hybrid orbitals produced equals the number of orbitals that have combined. Bonding with carbon sp^3 orbitals is illustrated in Figure 6-24(a) for a molecule of methane.

Hybridization also explains the bonding and geometry of many molecules formed by Group 15 and 16 elements. The sp^3 hybridization of a nitrogen atom ($[He]2s^22p^3$) yields four hybrid orbitals—one orbital containing a pair of electrons and three orbitals that each contain an unpaired electron. Each unpaired electron is capable of forming a single bond, as shown for ammonia in Figure 6-24(b). Similarly, two of the four sp^3 hybrid orbitals on an oxygen atom ($[He]2s^22p^4$) are occupied by two electron pairs and two are occupied by unpaired electrons. Each unpaired electron can form a single bond, as shown for water in Figure 6-24(c).

FIGURE 6-24 Bonds formed by the overlap of the 1*s* orbitals of hydrogen atoms and the sp^3 orbitals of (a) carbon, (b) nitrogen, and (c) oxygen. For the sake of clarity, only the hybrid orbitals of the central atoms are shown.



(a) Methane, CH_4 **(b)** Ammonia, NH_3 **(c)** Water, H_2O

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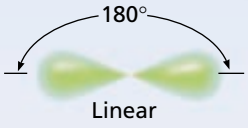
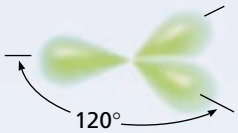
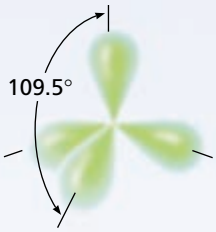
TABLE 6-6 Geometry of Hybrid Orbitals

Atomic orbitals	Type of hybridization	Number of hybrid orbitals	Geometry
s, *p*	*sp*	2	 Linear
s, *p*, *p*	sp^2	3	 Trigonal-planar
s, *p*, *p*, *p*	sp^3	4	 Tetrahedral

The linear geometry of molecules such as beryllium fluoride, BeF_2, (see Table 6-5 on page 186) is made possible by hybridization involving the *s* orbital and one available empty *p* orbital to yield *sp* hybrid orbitals. The trigonal-planar geometry of molecules such as boron fluoride, BF_3, is made possible by hybridization involving the *s* orbital, one singly occupied *p* orbital, and one empty *p* orbital to yield sp^2 hybrid orbitals. The geometries of *sp*, sp^2, and sp^3 hybrid orbitals are summarized in Table 6-6.

Intermolecular Forces

CHEMISTRY INTERACTIVE TUTOR
Module 4: Chemical Bonding

As a liquid is heated, the kinetic energy of its particles increases. At the boiling point, the energy is sufficient to overcome the force of attraction between the liquid's particles. The particles pull away from each other and enter the gas phase. Boiling point is therefore a good measure of the force of attraction between particles of a liquid. The higher the boiling point, the stronger the forces between particles.

The forces of attraction between molecules are known as **intermolecular forces.** Intermolecular forces vary in strength but are generally weaker than bonds that join atoms in molecules, ions in ionic compounds, or metal atoms in solid metals. Compare the boiling points of the metals and ionic compounds in Table 6-7 on page 190 with those of the molecular substances listed. Note that the values for ionic compounds and metals are much higher than those for molecular substances.

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TABLE 6-7 Boiling Points and Bonding Types

Bonding type	Substance	bp (1 atm, °C)
Nonpolar-covalent (molecular)	H_2	–253
	O_2	–183
	Cl_2	–34
	Br_2	59
	CH_4	–164
	CCl_4	77
	C_6H_6	80
Polar-covalent (molecular)	PH_3	–88
	NH_3	–33
	H_2S	–61
	H_2O	100
	HF	20
	HCl	–85
	ICl	97
Ionic	NaCl	1413
	MgF_2	2239
Metallic	Cu	2567
	Fe	2750
	W	5660

Molecular Polarity and Dipole-Dipole Forces

The strongest intermolecular forces exist between polar molecules. Polar molecules act as tiny dipoles because of their uneven charge distribution. *A* **dipole** *is created by equal but opposite charges that are separated by a short distance.* The direction of a dipole is from the dipole's positive pole to its negative pole. A dipole is represented by an arrow with a head pointing toward the negative pole and a crossed tail situated at the positive pole. The dipole created by a hydrogen chloride molecule, which has its negative end at the more electronegative chlorine atom, is indicated as follows.

$$\overset{+\longrightarrow}{\mathrm{H{-}Cl}}$$

The negative region in one polar molecule attracts the positive region in adjacent molecules, and so on throughout a liquid or solid. *The forces of attraction between polar molecules are known as* **dipole-dipole forces.** These forces are short-range forces, acting only between nearby molecules. The effect of dipole-dipole forces is reflected, for example, by the significant difference between the boiling points of bromine fluoride, Br−F, and fluorine, F−F. The boiling point of polar bromine fluoride is –20°C, whereas that of nonpolar fluorine is only –188°C. The dipole-dipole forces responsible for the relatively high boiling point of BrF are illustrated schematically in Figure 6-25.

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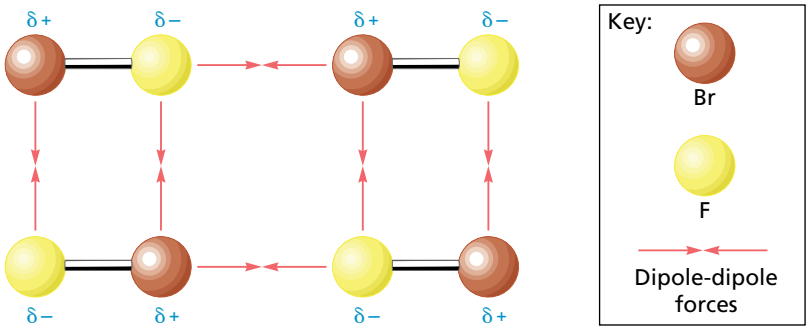
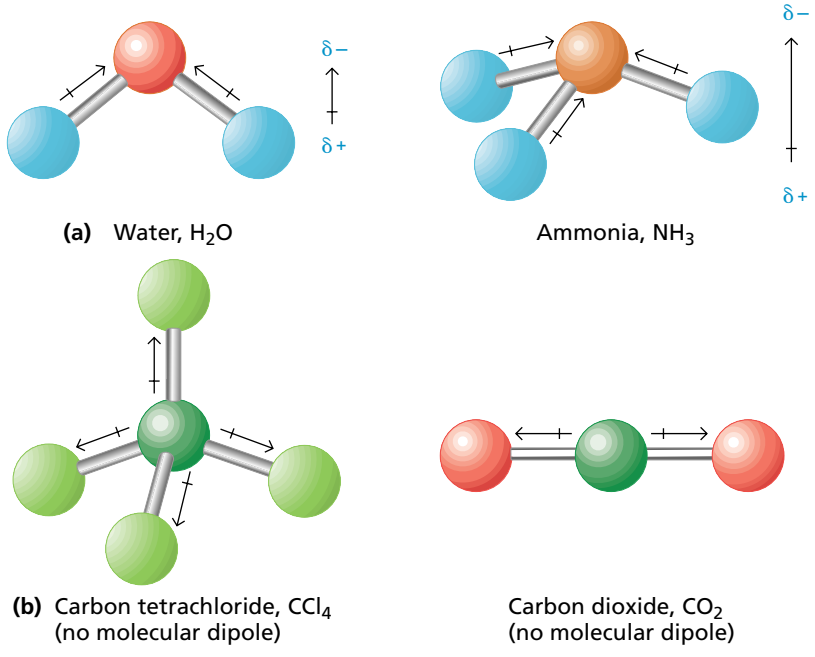


FIGURE 6-25 Ball-and-stick models illustrate the dipole-dipole forces between molecules of bromine fluoride, BrF. In each molecule, the highly electronegative fluorine atom has a partial negative charge, leaving each bromine atom with a partial positive charge. Consequently, the negative and positive ends of neighboring molecules attract each other.

The polarity of diatomic molecules such as BrF is determined by just one bond. For molecules containing more than two atoms, molecular polarity depends on both the polarity and the orientation of each bond. A molecule of water, for example, has two hydrogen-oxygen bonds in which the more-electronegative oxygen atom is the negative pole of each bond. Because the molecule is bent, the polarities of these two bonds combine to make the molecule highly polar, as shown in Figure 6-26. An ammonia molecule is also highly polar because the dipoles of the three nitrogen-hydrogen bonds are additive, combining to create a net molecular dipole. In some molecules, individual bond dipoles cancel one another, causing the resulting molecular polarity to be zero. Carbon dioxide and carbon tetrachloride are molecules of this type.

A polar molecule can *induce* a dipole in a nonpolar molecule by temporarily attracting its electrons. The result is a short-range intermolecular force that is somewhat weaker than the dipole-dipole force. The force of an induced dipole accounts for the solubility of nonpolar O_2 in water. The positive pole of a water molecule attracts the outer electrons



(a) Water, H_2O

Ammonia, NH_3

(b) Carbon tetrachloride, CCl_4 (no molecular dipole)

Carbon dioxide, CO_2 (no molecular dipole)

FIGURE 6-26 (a) The bond polarities in a water or an ammonia molecule are additive, causing the molecule as a whole to be polar. (b) In molecules of carbon tetrachloride and carbon dioxide, the bond polarities extend equally and symmetrically in different directions, canceling each other's effect and causing each molecule as a whole to be nonpolar.

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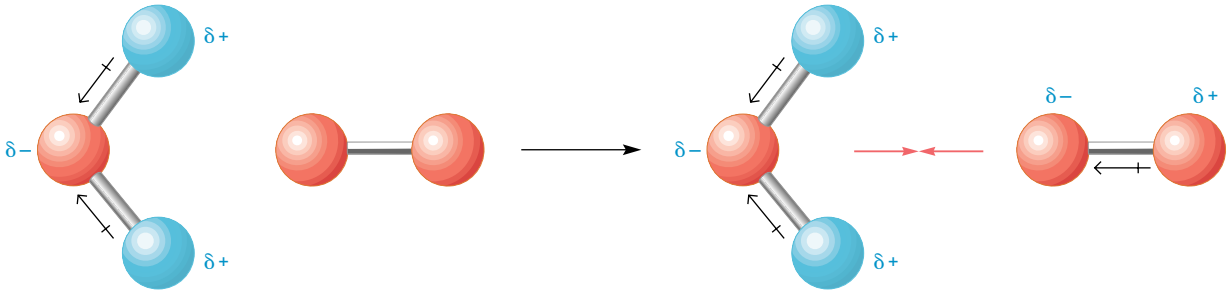

FIGURE 6-27 Dipole-induced dipole interaction. The positive pole of a water molecule causes a temporary change in the electron distribution of an oxygen molecule. The negative pole induced in the oxygen molecule is then attracted to the positive pole of the water molecule.

of an adjacent oxygen molecule. The oxygen molecule, then, has an induced negative pole on the side toward the water molecule and an induced positive pole on the opposite side. The result is an attraction to the water molecule, as shown in Figure 6-27.

Hydrogen Bonding

Some hydrogen-containing compounds, such as hydrogen fluoride (HF), water (H_2O), and ammonia (NH_3), have unusually high boiling points. This is explained by the presence of a particularly strong type of dipole-dipole force. In compounds containing H—F, H—O, or H—N bonds, the large electronegativity differences between hydrogen atoms and fluorine, oxygen, or nitrogen atoms make the bonds connecting them highly polar. This gives the hydrogen atom a positive charge that is almost half as large as that of a proton. Moreover, the small size of the hydrogen atom allows the atom to come very close to an unshared pair of electrons on an adjacent molecule. *The intermolecular force in which a hydrogen atom that is bonded to a highly electronegative atom is attracted to an unshared pair of electrons of an electronegative atom in a nearby molecule is known as* **hydrogen bonding.**

Hydrogen bonds are usually represented by dotted lines connecting the hydrogen-bonded hydrogen to the unshared electron pair of the electronegative atom to which it is attracted, as illustrated for water in Figure 6-28. The effect of hydrogen bonding can be seen by comparing the boiling points in Table 6-7 on page 190. Look at phosphine, PH_3, compared with hydrogen-bonded ammonia, NH_3. How does hydrogen sulfide, H_2S, compare with strongly hydrogen-bonded water, H_2O?

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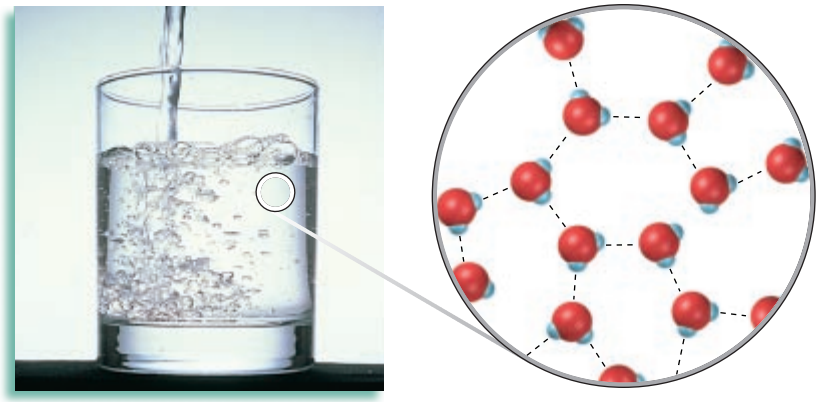

FIGURE 6-28 Space-filling models illustrate hydrogen bonding between water molecules. The dotted lines indicate the attraction between electronegative oxygen atoms and electropositive hydrogen atoms of neighboring molecules.

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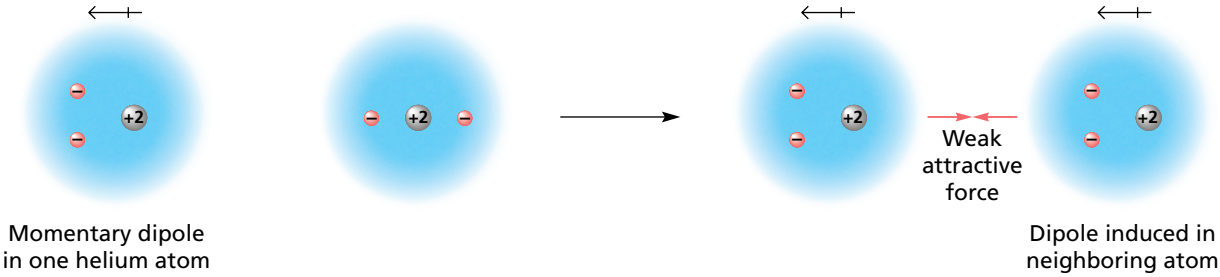

FIGURE 6-29 When an instantaneous, temporary dipole develops in a helium atom, it induces a dipole in a neighboring atom.

London Dispersion Forces

Even noble-gas atoms and molecules that are nonpolar experience a weak intermolecular attraction. In any atom or molecule—polar or nonpolar—the electrons are in continuous motion. As a result, at any instant the electron distribution may be slightly uneven. The momentary, uneven charge creates a positive pole in one part of the atom or molecule and a negative pole in another. This temporary dipole can then induce a dipole in an adjacent atom or molecule. The two are held together for an instant by the weak attraction between the temporary dipoles, as illustrated in Figure 6-29. *The intermolecular attractions resulting from the constant motion of electrons and the creation of instantaneous dipoles are called* **London dispersion forces,** after Fritz London, who first proposed their existence in 1930.

London forces act between all atoms and molecules. But they are the *only* intermolecular forces acting among noble-gas atoms and nonpolar molecules. This fact is reflected in the low boiling points of the noble gases and nonpolar molecular compounds listed in Table 6-7 on page 190. Because London forces are dependent on the motion of electrons, their strength increases with the number of electrons in the interacting atoms or molecules. In other words, London forces increase with increasing atomic or molar mass. This trend can be seen by comparing the boiling points of the gases helium, He, and argon, Ar; hydrogen, H_2, and oxygen, O_2; and chlorine, Cl_2, and bromine, Br_2.

SECTION REVIEW

1. What two theories can be used to predict molecular geometry?
2. Draw the Lewis structure, and use the VSEPR theory to predict the molecular geometry of the following molecules:
   a. SO_2 b. CI_4 c. BCl_3
3. What are some factors that affect the geometry of a molecule?
4. Explain what is meant by sp^3 hybridization.
5. What type of intermolecular force contributes to the high boiling point of water? Explain.

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CHAPTER 6 REVIEW

CHAPTER SUMMARY

6-1

- Most atoms are chemically bonded to other atoms.
- The three major types of chemical bonding are ionic, covalent, and metallic.
- In general, atoms of metals bond ionically with atoms of nonmetals, atoms of metals bond metallically with each other, and atoms of nonmetals bond covalently with each other.

Vocabulary

chemical bond (161)
covalent bonding (161)
ionic bonding (161)
nonpolar-covalent bond (162)
polar (162)
polar-covalent bond (162)

6-2

- Atoms in molecules are joined by covalent bonds.
- The bond length between two atoms in a molecule is the distance at which the potential energy of the bonded atoms is minimized.
- The octet rule states that many chemical compounds tend to form bonds so that each atom, by gaining, losing, or sharing electrons, shares or has eight electrons in its highest occupied energy level.
- A single bond is a covalent bond in which a pair of electrons is shared between two atoms. Covalent bonds in which more than one pair of electrons is shared are called multiple bonds.
- Bonding within many molecules and ions can be indicated by a Lewis structure. Molecules or ions that cannot be correctly represented by a single Lewis structure are represented by resonance structures.

Vocabulary

bond energy (167)
bond length (167)
chemical formula (164)
diatomic molecule (164)
double bond (172)
electron-dot notation (170)
Lewis structures (171)
lone pair (171)
molecular compound (164)
molecular formula (164)
molecule (164)
multiple bond (173)
octet rule (169)
resonance (175)
single bond (171)
structural formula (171)
triple bond (173)
unshared pair (171)

6-3

- An ionic compound is a three-dimensional network of positive and negative ions mutually attracted to one another.
- Because of the strong attraction between positive and negative ions, ionic compounds tend to be harder and more brittle and to have higher boiling points than materials containing only covalently bonded atoms.
- Polyatomic ions are charged groups of atoms held together by covalent bonds.

Vocabulary

formula unit (176)
ionic compound (176)
lattice energy (178)
polyatomic ion (180)

6-4

- Metallic bonding is a type of chemical bonding that results from the attraction between metal atoms and a surrounding sea of mobile electrons.
- The electron sea formed in metallic bonding gives metals their properties of high electrical and thermal conductivity, malleability, ductility, and luster.

Vocabulary

ductility (182)
malleability (182)
metallic bonding (181)

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CHAPTER SUMMARY (continued)

6-5

- VSEPR theory is used to predict the shapes of molecules based on the fact that electron pairs strongly repel each other and tend to be oriented as far apart as possible.
- Hybridization theory is used to predict the shapes of molecules based on the fact that orbitals within an atom can mix to form orbitals of equal energy.
- Intermolecular forces, such as dipole-dipole forces and London dispersion forces, exist between certain types of molecules. Hydrogen bonding is a special case of dipole-dipole forces.

Vocabulary

dipole (190)
dipole-dipole forces (190)
hybrid orbitals (188)
hybridization (187)
hydrogen bonding (192)
intermolecular forces (189)
London dispersion forces (193)
molecular polarity (183)
VSEPR theory (183)

REVIEWING CONCEPTS

1. What is a chemical bond? (6-1)

2. Identify and define the three major types of chemical bonding. (6-1)

3. What is the relationship between electronegativity and the ionic character of a chemical bond? (6-1)

4. a. What is the meaning of the term *polar,* as applied to chemical bonding?
b. Distinguish between polar-covalent and nonpolar-covalent bonds. (6-1)

5. In general, what determines whether atoms will form chemical bonds? (6-1)

6. What is a molecule? (6-2)

7. a. What determines bond length?
b. In general, how are bond energies and bond lengths related? (6-2)

8. Describe the general location of the electrons in a covalent bond. (6-2)

9. As applied to covalent bonding, what is meant by an unshared or lone pair of electrons? (6-2)

10. Describe the octet rule in terms of noble-gas configurations and potential energy. (6-2)

11. Determine the number of valence electrons in an atom of each of the following elements:
a. H b. F
c. Mg d. O
e. Al f. N
g. C (6-2)

12. When drawing Lewis structures, which atom is usually the central atom? (6-2)

13. Distinguish between single, double, and triple covalent bonds by defining each and providing an illustration of each type. (6-2)

14. In writing Lewis structures, how is the need for multiple bonds generally determined? (6-2)

15. a. What is an ionic compound?
b. In what form do most ionic compounds occur? (6-3)

16. a. What is a formula unit?
b. What are the components of one formula unit of CaF_2? (6-3)

17. a. What is lattice energy?
b. In general, what is the relationship between lattice energy and the strength of ionic bonding? (6-3)

18. a. In general, how do ionic and molecular compounds compare in terms of melting points, boiling points, and ease of vaporization?
b. What accounts for the observed differences in the properties of ionic and molecular compounds?
c. Cite three physical properties of ionic compounds. (6-3)

19. a. What is a polyatomic ion?
b. Give two examples of polyatomic ions.

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c. In what form do such ions often occur in nature? (6-3)

20. a. How do the properties of metals differ from those of both ionic and molecular compounds?
b. What specific property of metals accounts for their unusual electrical conductivity? (6-4)

21. What properties of metals contribute to their tendency to form metallic bonds? (6-4)

22. a. What is metallic bonding?
b. How can the strength of metallic bonding be measured? (6-4)

23. a. How is the VSEPR theory used to classify molecules?
b. What molecular geometry would be expected for F_2 and HF? (6-5)

24. According to the VSEPR theory, what molecular geometries are associated with the following types of molecules?
a. AB_2
b. AB_3
c. AB_4
d. AB_5
e. AB_6 (6-5)

25. Describe the role of each of the following in predicting molecular geometries:
a. unshared electron pairs
b. double bonds (6-5)

26. a. What are hybrid orbitals?
b. What determines the number of hybrid orbitals produced by an atom? (6-5)

27. a. What are intermolecular forces?
b. In general, how do these forces compare in strength with those in ionic and metallic bonding?
c. Where are the strongest intermolecular forces found? (6-5)

28. What is the relationship between electronegativity and the polarity of a chemical bond? (6-5)

29. a. What are dipole-dipole forces?
b. What determines the polarity of a molecule? (6-5)

30. a. What is meant by an induced dipole?
b. What is the everyday importance of this type of intermolecular force? (6-5)

31. a. What is hydrogen bonding?
b. What accounts for its extraordinary strength? (6-5)

32. What are London dispersion forces? (6-5)

PROBLEMS

Chemical Bond Character

33. Determine the electronegativity difference, the probable bond type, and the more-electronegative atom with respect to bonds formed between the following pairs of atoms. (Hint: See Sample Problem 6-1.)
a. H and I
b. S and O
c. K and Br
d. Si and Cl
e. H and F
f. Se and S
g. C and H

34. List the bonding pairs described in item 33 in order of increasing covalent character.

35. Use orbital notation to illustrate the bonding in each of the following molecules:
a. chlorine, Cl_2
b. oxygen, O_2
c. hydrogen fluoride, HF

36. The lattice energy of sodium chloride, NaCl, is –787.5 kJ/mol. The lattice energy of potassium chloride, KCl, is –715 kJ/mol. In which compound is the bonding between ions stronger? Why?

Electron-Dot Notation and Lewis Structures

37. Use electron-dot notation to illustrate the number of valence electrons present in one atom of each of the following elements. (Hint: See Sample Problem 6-2.)
a. Li
b. Ca
c. Cl
d. O

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e. C
f. P
g. Al
h. S

38. Use electron-dot structures to demonstrate the formation of ionic compounds involving the following elements:
a. Na and S
b. Ca and O
c. Al and S

39. Draw Lewis structures for each of the following molecules. (Hint: See Sample Problem 6-4.)
a. contains one C and four F atoms
b. contains two H and one Se atom
c. contains one N and three I atoms
d. contains one Si and four Br atoms
e. contains one C, one Cl, and three H atoms

40. Determine the type of hybrid orbitals formed by the boron atom in a molecule of boron fluoride, BF_3. (Hint: See Sample Problems 6-5 and 6-6.)

41. Draw Lewis structures for each of the following molecules. Show resonance structures, if they exist.
a. O_2
b. N_2
c. CO
d. SO_2

42. Draw Lewis structures for each of the following polyatomic ions. Show resonance structures, if they exist.
a. OH^-
b. $H_3C_2O_2^-$
c. BrO_3^-

VSEPR Theory and Molecular Geometry

43. According to the VSEPR theory, what molecular geometries are associated with the following types of molecules?
a. AB_3E
b. AB_2E_2
c. AB_2E

44. Use hybridization to explain the bonding in methane, CH_4.

45. For each of the following polar molecules, indicate the direction of the resulting dipole:
a. H–F
b. H–Cl
c. H–Br
d. H–I

46. Determine whether each of the following bonds would be polar or nonpolar:
a. H–H
b. H–O
c. H–F
d. Br–Br
e. H–Cl
f. H–N

47. On the basis of individual bond polarity and orientation, determine whether each of the following molecules would be polar or nonpolar:
a. H_2O
b. I_2
c. CF_4
d. NH_3
e. CO_2

48. Draw a Lewis structure for each of the following molecules, and then use the VSEPR theory to predict the molecular geometry of each:
a. SCl_2
b. PI_3
c. Cl_2O
d. NH_2Cl
e. $SiCl_3Br$
f. ONCl

49. Draw a Lewis structure for each of the following polyatomic ions, and then use VSEPR theory to determine the geometry of each:
a. NO_3^-
b. NH_4^+
c. SO_4^{2-}
d. ClO_2^-

MIXED REVIEW

50. Arrange the following pairs from strongest to weakest attraction:
a. polar molecule and polar molecule
b. nonpolar molecule and nonpolar molecule
c. polar molecule and ion
d. ion and ion

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51. Determine the geometry of the following molecules:
a. CCl_4
b. $BeCl_2$
c. PH_3

52. What types of atoms tend to form the following types of bonding?
a. ionic
b. covalent
c. metallic

53. What happens to the energy level and stability of two bonded atoms when they are separated and become individual atoms?

54. Draw the three resonance structures for sulfur trioxide, SO_3.

55. a. How do ionic and covalent bonding differ?
b. How does an ionic compound differ from a molecular compound?
c. How does an ionic compound differ from a metal?

56. Write the electron-dot notation for each of the following elements:
a. He
b. Cl
c. O
d. P
e. B

57. Write the structural formula for methanol, CH_3OH.

58. How many K^+ and S^{2-} ions would be in one formula unit of the ionic compound formed by these ions?

59. Explain metallic bonding in terms of the sparsely populated outermost orbitals of metal atoms.

60. Explain the role of molecular geometry in determining molecular polarity.

61. How does the energy level of a hybrid orbital compare with the energy levels of the orbitals it was formed from?

62. Aluminum's heat of vaporization is 284 kJ/mol. Beryllium's heat of vaporization is 224 kJ/mol. In which element is the bonding stronger between atoms?

63. Determine the electronegativity difference, the probable bonding type, and the more-electronegative atom for each of the following pairs of atoms:
a. Zn and O
b. Br and I
c. S and Cl

64. Draw the Lewis structure for each of the following molecules:
a. PCl_3
b. CCl_2F_2
c. CH_3NH_2

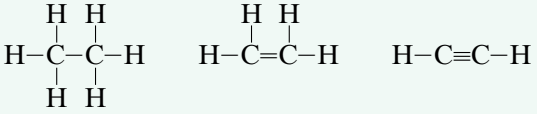
65. Write the Lewis structure for $BeCl_2$. (Hint: Beryllium atoms do not follow the octet rule.)

66. Draw a Lewis structure for each of the following polyatomic ions and determine their geometries:
a. NO_2^-
b. NO_3^-
c. NH_4^+

67. Why are most atoms chemically bonded to other atoms in nature?

CRITICAL THINKING

68. Inferring Relationships The length of a bond varies depending on the type of bond formed. Predict and compare the lengths of the carbon-carbon bonds in the following molecules. Explain your answer. (Hint: See Table 6-2.)



C_2H_6 C_2H_4 C_2H_2

TECHNOLOGY & LEARNING

69. Graphing Calculator Classify Bonding Type According to Difference in Electronegativity

The graphing calculator can run a program that classifies bonding between atoms according to the difference between the atoms' electronegativities. Use this program to determine the electronegativity difference between the bonded atoms and to classify bonding type.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data sets and run the application as directed. If you are using another calculator, your teacher will

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provide you with the keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. Which element pair(s) has/have a pure covalent bond?
b. What type of bond does the pair H, O have?
c. What type of bond does the pair Ca, O have?

HANDBOOK SEARCH

70. Figure 6-18 on page 181 shows a model for a body-centered cubic crystal. Review the Properties tables for all of the metals in the *Elements Handbook* (pages 728–749). What metals exist in body-centered cubic structures?

71. Group 14 of the *Elements Handbook* (pages 754–769) contains a discussion of the band theory of metals. How does this model explain the electrical conductivity of metals?

RESEARCH & WRITING

72. Prepare a report on the work of Linus Pauling.
a. Discuss his work on the nature of the chemical bond.
b. Linus Pauling was an advocate of the use of vitamin C as a preventative for colds. Evaluate Pauling's claims. Determine if there is any scientific evidence that indicates whether vitamin C helps prevent colds.

73. Covalently bonded solids, such as silicon, an element used in computer components, are harder than pure metals. Research theories that explain the hardness of covalently bonded solids and their usefulness in the computer industry. Present your findings to the class.

ALTERNATIVE ASSESSMENT

74. Devise a set of criteria that will allow you to classify the following substances as ionic or nonionic: $CaCO_3$, Cu, H_2O, NaBr, and C (graphite). Show your criteria to your instructor.

75. **Performance Assessment** Identify 10 common substances in and around your home, and indicate whether you would expect these substances to contain ionic, covalent, or metallic bonds.

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CHAPTER 7

Chemical Formulas and Chemical Compounds

Chemists use chemical names and formulas to describe the atomic composition of compounds.

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Chemical Names and Formulas

SECTION 7-1

Objectives

- Explain the significance of a chemical formula.
- Determine the formula of an ionic compound formed between two given ions.
- Name an ionic compound given its formula.
- Using prefixes, name a binary molecular compound from its formula.
- Write the formula of a binary molecular compound given its name.

The total number of natural and synthetic chemical compounds runs in the millions. For some of these substances, certain common names remain in everyday use. For example, calcium carbonate is better known as limestone, and sodium chloride is usually referred to simply as table salt. And everyone recognizes dihydrogen monoxide by its popular name, water.

Unfortunately, common names usually give no information about chemical composition. To describe the atomic makeup of compounds, chemists use systematic methods for naming compounds and for writing chemical formulas. In this chapter, you will be introduced to some of the rules used to identify simple chemical compounds.

Significance of a Chemical Formula

Recall that a chemical formula indicates the relative number of atoms of each kind in a chemical compound. For a molecular compound, the chemical formula reveals the number of atoms of each element contained in a single molecule of the compound, as shown below for the hydrocarbon octane. (*Hydrocarbons* are molecular compounds composed solely of carbon and hydrogen.)

C_8H_{18}

Subscript indicates that there are 8 carbon atoms in a molecule of octane.

Subscript indicates that there are 18 hydrogen atoms in a molecule of octane.

Unlike a molecular compound, an ionic compound consists of a lattice of positive and negative ions held together by mutual attraction. The chemical formula for an ionic compound represents one formula unit—the simplest ratio of the compound's positive ions (cations) and its negative ions (anions). The chemical formula for aluminum sulfate, an ionic compound consisting of aluminum cations and polyatomic sulfate anions, is written as shown on page 204.

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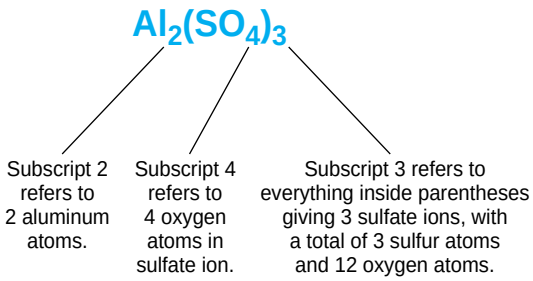
$Al_2(SO_4)_3$
Subscript 2 refers to 2 aluminum atoms.
Subscript 4 refers to 4 oxygen atoms in sulfate ion.
Subscript 3 refers to everything inside parentheses giving 3 sulfate ions, with a total of 3 sulfur atoms and 12 oxygen atoms.

Note how the parentheses are used. They surround the polyatomic anion to identify it as a unit. The subscript 3 refers to the entire unit. Notice also that there is no subscript written next to the symbol for sulfur. When there is no subscript written next to an atom's symbol, the value of the subscript is understood to be 1.

Monatomic Ions

By gaining or losing electrons, many main-group elements form ions with noble-gas configurations. For example, Group 1 metals lose one electron to give 1+ cations, such as Na^+. Group 2 metals lose two electrons to give 2+ cations, such as Mg^{2+}. *Ions formed from a single atom are known as* **monatomic ions.** The nonmetals of Groups 15, 16, and 17 gain electrons to form anions. For example, in ionic compounds nitrogen forms the 3– anion, N^{3-}. The three added electrons plus the five outermost electrons in nitrogen atoms give a completed outermost octet. Similarly, the Group 16 elements oxygen and sulfur form 2– anions, and the Group 17 halogens form 1– anions.

Not all main-group elements readily form ions, however. Rather than gain or lose electrons, atoms of carbon and silicon form covalent bonds in which they share electrons with other atoms. Other elements tend to form ions that do not have noble-gas configurations. For instance, it is difficult for the Group 14 metals tin and lead to lose four electrons to achieve a noble-gas configuration. Instead, they tend to lose the two electrons in their outer *p* orbitals but retain the two electrons in their outer *s* orbitals to form 2+ cations. (Tin and lead can also form molecular compounds in which all four valence electrons are involved in covalent bonding.)

Elements from the *d*-block form 2+, 3+, or, in a few cases, 1+ or 4+ cations. Many *d*-block elements form two ions of different charges. For example, copper forms 1+ cations and 2+ cations. Iron and chromium, on the other hand, each form 2+ cations as well as 3+ cations. And vanadium and lead form 2+, 3+, and 4+ cations.

Naming cations

K^+

Potassium cation

Mg^{2+}

Magnesium cation

Naming Monatomic Ions

Monatomic cations are identified simply by the element's name, as illustrated by the examples at left. Naming monatomic anions is slightly more

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complicated. First, the ending of the element's name is dropped. Then the ending *-ide* is added to the root name, as illustrated by the examples at right.

The names and symbols of the common monatomic cations and anions are organized according to their charges in Table 7-1. The names of many of the ions in the table include Roman numerals. These numerals are part of the *Stock system* of naming chemical ions and elements. You will read more about the Stock system and other systems of naming chemicals later in this chapter.

Naming anions

F	F^-
Fluor*ine*	Fluor*ide* anion
N	N^{3-}
Nitr*ogen*	Nitr*ide* anion

TABLE 7-1 *Some Common Monatomic Ions*

Main-group elements

1+		2+		3+		
lithium	Li^+					
sodium	Na^+	magnesium	Mg^{2+}	aluminum	Al^{3+}	
potassium	K^+	calcium	Ca^{2+}			
rubidium	Rb^+	strontium	Sr^{2+}			
cesium	Cs^+	barium	Ba^{2+}			
1–		**2–**		**3–**		
fluoride	F^-	oxide	O^{2-}	nitride	N^{3-}	
chloride	Cl^-	sulfide	S^{2-}			
bromide	Br^-					
iodide	I^-					

***d*-Block elements and others with multiple ions**

1+		2+		3+		4+	
copper(I)	Cu^+	cadmium	Cd^{2+}	chromium(III)	Cr^{3+}	lead(IV)	Pb^{4+}
silver	Ag^+	chromium(II)	Cr^{2+}	iron(III)	Fe^{3+}	vanadium(IV)	V^{4+}
		cobalt(II)	Co^{2+}	vanadium(III)	V^{3+}	tin(IV)	Sn^{4+}
		copper(II)	Cu^{2+}				
		iron(II)	Fe^{2+}				
		lead(II)	Pb^{2+}				
		manganese(II)	Mn^{2+}				
		mercury(II)	Hg^{2+}				
		nickel(II)	Ni^{2+}				
		tin(II)	Sn^{2+}				
		vanadium(II)	V^{2+}				
		zinc	Zn^{2+}				

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Binary Ionic Compounds

Compounds composed of two different elements are known as **binary compounds.** In a binary ionic compound, the total numbers of positive charges and negative charges must be equal. Therefore, the formula for such a compound can be written given the identities of the compound's ions. For example, magnesium and bromine combine to form the ionic compound magnesium bromide. Magnesium, a Group 2 metal, forms the Mg^{2+} cation. Note that the $^{2+}$ in Mg^{2+} is written as a superscript. Bromine, a halogen, forms the Br^- anion when combined with a metal. In each formula unit of magnesium bromide, two Br^- anions are required to balance the 2+ charge of the Mg^{2+} cation. The compound's formula must therefore indicate one Mg^{2+} cation and two Br^- anions. The symbol for the cation is written first.

Ions combined: Mg^{2+}, Br^-, Br^- *Chemical formula:* $MgBr_2$

Note that the $_2$ in Br_2 is written as a subscript. The charges of the ions are not included in the formula. This is usually the case when writing formulas for binary ionic compounds.

As an aid to determining subscripts in formulas for ionic compounds, the positive and negative charges can be "crossed over." Crossing over is a method of balancing the charges between ions in an ionic compound. For example, the formula for the compound formed by the aluminum ion, Al^{3+}, and the oxide ion, O^{2-}, is determined as follows.

1. *Write the symbols for the ions side by side. Write the cation first.*

$$Al^{3+}\ O^{2-}$$

2. *Cross over the charges by using the absolute value of each ion's charge as the subscript for the other ion.*

$$Al_2^{3+}\ O_3^{2-}$$

3. *Check the subscripts and divide them by their largest common factor to give the smallest possible whole-number ratio of ions. Then write the formula.*
   Multiplying the charge by the subscript shows that the charge on two Al^{3+} cations ($2 \times 3+ = 6+$) equals the charge on three O^{2-} anions ($3 \times 2- = 6-$). The largest common factor of the subscripts is 1. The correct formula is therefore written as follows.

$$Al_2O_3$$

Naming Binary Ionic Compounds

The **nomenclature,** *or naming system,* of binary ionic compounds involves combining the names of the compound's positive and negative

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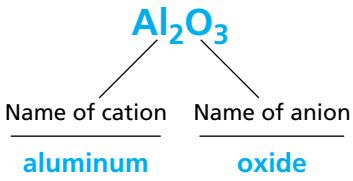
ions. The name of the cation is given first, followed by the name of the anion. For most simple ionic compounds, the ratio of the ions is not indicated in the compound's name because it is understood based on the relative charges of the compound's ions. The naming of a simple binary ionic compound is illustrated below.



SAMPLE PROBLEM 7-1

Write the formulas for the binary ionic compounds formed between the following elements:
a. zinc and iodine **b. zinc and sulfur**

SOLUTION

Write the symbols for the ions side by side. Write the cation first.

a. Zn^{2+} I^-
b. Zn^{2+} S^{2-}

Cross over the charges to give subscripts.

a. Zn_1^{2+} I_2^-
b. Zn_2^{2+} S_2^{2-}

Check the subscripts and divide them by their largest common factor to give the smallest possible whole-number ratio of ions. Then write the formula.

a. The subscripts are mathematically correct because they give equal total charges of $1 \times 2+ = 2+$ and $2 \times 1- = 2-$. The largest common factor of the subscripts is 1. The smallest possible whole-number ratio of ions in the compound is therefore 1:2. *The subscript 1 is not written,* so the formula is ZnI_2.

b. The subscripts are mathematically correct because they give equal total charges of $2 \times 2+ = 4+$ and $2 \times 2- = 4-$. The largest common factor of the subscripts is 2. The smallest whole-number ratio of ions in the compound is therefore 1:1. The correct formula is ZnS.

PRACTICE

1. Write formulas for the binary ionic compounds formed between the following elements:
a. potassium and iodine
b. magnesium and chlorine
c. sodium and sulfur
d. aluminum and sulfur
e. aluminum and nitrogen

Answer
1. a. KI
b. $MgCl_2$
c. Na_2S
d. Al_2S_3
e. AlN

2. Name the binary ionic compounds indicated by the following formulas:
a. AgCl
b. ZnO
c. $CaBr_2$
d. SrF_2
e. BaO
f. $CaCl_2$

2. a. silver chloride
b. zinc oxide
c. calcium bromide
d. strontium fluoride
e. barium oxide
f. calcium chloride

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The Stock System of Nomenclature

Some elements, such as iron, form two or more cations with different charges. To distinguish the ions formed by such elements, the Stock system of nomenclature is used. This system uses a Roman numeral to indicate an ion's charge. The numeral is enclosed in parentheses and placed *immediately* after the metal name.

Fe^{2+}	Fe^{3+}
iron(II)	iron(III)

Names of metals that commonly form only one cation *do not* include a Roman numeral.

Na^{+}	Ba^{2+}	Al^{3+}
sodium	barium	aluminum

There is no element that commonly forms more than one monatomic anion.

Naming a binary ionic compound according to the Stock system is illustrated below.

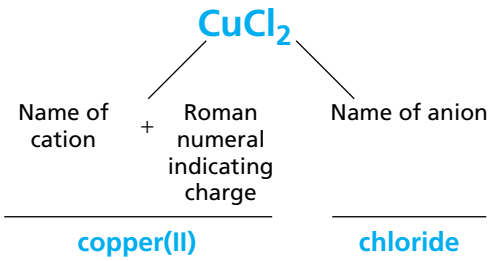

FIGURE 7-1 Different cations of the same metal form different compounds even when they combine with the same anion. Compare (a) lead(IV) oxide, PbO_2, with (b) lead(II) oxide, PbO.

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SAMPLE PROBLEM 7-2

Write the formula and give the name for the compound formed by the ions Cr^{3+} and F^-.

SOLUTION

Write the symbols for the ions side by side. Write the cation first.

$$Cr^{3+}\ F^-$$

Cross over the charges to give subscripts.

$$Cr_1^{3+}\ F_3^-$$

Check the subscripts and write the formula.

The subscripts are correct because they give charges of $1 \times 3+ = 3+$ and $3 \times 1- = 3-$. The largest common factor of the subscripts is 1, so the smallest whole-number ratio of the ions is 1:3. The formula is therefore CrF_3. As Table 7-1 on page 205 shows, chromium forms more than one ion. Therefore, the name of the 3+ chromium ion must be followed by a Roman numeral indicating its charge. The compound's name is chromium(III) fluoride.

PRACTICE

1. Write the formula and give the name for the compounds formed between the following ions:
   a. Cu^{2+} and Br^-
   b. Fe^{2+} and O^{2-}
   c. Pb^{2+} and Cl^-
   d. Hg^{2+} and S^{2-}
   e. Sn^{2+} and F^-
   f. Fe^{3+} and O^{2-}

2. Give the names for the following compounds:
   a. CuO
   b. CoF_3
   c. SnI_4
   d. FeS

Answer

1. a. $CuBr_2$, copper(II) bromide
   b. FeO, iron(II) oxide
   c. $PbCl_2$, lead(II) chloride
   d. HgS, mercury(II) sulfide
   e. SnF_2, tin(II) fluoride
   f. Fe_2O_3, iron(III) oxide

2. a. copper(II) oxide
   b. cobalt(III) fluoride
   c. tin(IV) iodide
   d. iron(II) sulfide

Compounds Containing Polyatomic Ions

Table 7-2 on page 210 lists some common polyatomic ions. All but the ammonium ion are negatively charged and most are **oxyanions**—*polyatomic ions that contain oxygen.* In several cases, two different oxyanions are formed by the same two elements. Nitrogen and oxygen, for example, are combined in both NO_3^- and NO_2^-. When naming compounds containing such oxyanions, the most common ion is given the ending *-ate.* The ion with one less oxygen atom is given the ending *-ite.*

NO_2^-	NO_3^-
nitrite	nitrate

Sometimes two elements form more than two different oxyanions. In this case, an anion with one less oxygen than the *-ite* anion is given the

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TABLE 7-2 Some Polyatomic Ions

1+		2+			
ammonium	NH_4^+	dimercury*	Hg_2^{2+}		

1–		2–		3–	
acetate	CH_3COO^-	carbonate	CO_3^{2-}	phosphate	PO_4^{3-}
bromate	BrO_3^-	chromate	CrO_4^{2-}	arsenate	AsO_4^{3-}
chlorate	ClO_3^-	dichromate	$Cr_2O_7^{2-}$		
chlorite	ClO_2^-	hydrogen phosphate	HPO_4^{2-}		
cyanide	CN^-	oxalate	$C_2O_4^{2-}$		
dihydrogen phosphate	$H_2PO_4^-$	peroxide	O_2^{2-}		
hydrogen carbonate (bicarbonate)	HCO_3^-	sulfate	SO_4^{2-}		
hydrogen sulfate	HSO_4^-	sulfite	SO_3^{2-}		
hydroxide	OH^-				
hypochlorite	ClO^-				
nitrate	NO_3^-				
nitrite	NO_2^-				
perchlorate	ClO_4^-				
permanganate	MnO_4^-				

*The mercury(I) cation exists as two Hg^+ ions joined together by a covalent bond and is written as Hg_2^{2+}.

prefix *hypo-*. An anion with one more oxygen than the *-ate* anion is given the prefix *per-*. This nomenclature is illustrated by the four oxyanions formed between chlorine and oxygen.

ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
hypochlorite	chlorite	chlorate	perchlorate

Compounds containing polyatomic ions are named in the same manner as binary ionic compounds. The name of the cation is given first, followed by the name of the anion. For example, the two compounds formed with silver by the nitrate and nitrite anions are named silver nitrate, $AgNO_3$, and silver nitrite, $AgNO_2$, respectively. When more than one polyatomic ion is present in a compound, the formula for the entire ion is surrounded by parentheses. This is illustrated on page 204 for aluminum sulfate, $Al_2(SO_4)_3$. The formula indicates that an aluminum sulfate formula unit has 2 aluminum cations and 3 sulfate anions.

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SAMPLE PROBLEM 7-3

Write the formula for tin(IV) sulfate.

SOLUTION

Write the symbols for the ions side by side. Write the cation first.

$$Sn^{4+}\ SO_4^{2-}$$

Cross over the charges to give subscripts. Add parentheses around the polyatomic ion if necessary.

$$Sn_2^{4+}\ (SO_4)_4^{2-}$$

Check the subscripts and write the formula.
The total positive charge is $2 \times 4+ = 8+$. The total negative charge is $4 \times 2- = 8-$. The charges are equal. The largest common factor of the subscripts is 2, so the smallest whole-number ratio of ions in the compound is 1:2. The correct formula is therefore $Sn(SO_4)_2$.

PRACTICE

1. Write formulas for the following ionic compounds:
   a. sodium iodide
   b. calcium chloride
   c. potassium sulfide
   d. lithium nitrate
   e. copper(II) sulfate
   f. sodium carbonate
   g. calcium nitrite
   h. potassium perchlorate

2. Give the names for the following compounds:
   a. Ag_2O
   b. $Ca(OH)_2$
   c. $KClO_3$
   d. NH_4OH
   e. $FeCrO_4$
   f. $KClO$

Answer

1. a. NaI
   b. $CaCl_2$
   c. K_2S
   d. $LiNO_3$
   e. $CuSO_4$
   f. Na_2CO_3
   g. $Ca(NO_2)_2$
   h. $KClO_4$

2. a. silver oxide
   b. calcium hydroxide
   c. potassium chlorate
   d. ammonium hydroxide
   e. iron(II) chromate
   f. potassium hypochlorite

Naming Binary Molecular Compounds

Unlike ionic compounds, molecular compounds are composed of individual covalently bonded units, or molecules. Chemists use two nomenclature systems to name binary molecules. The newer system is the Stock system for naming molecular compounds, which requires an understanding of oxidation numbers. This system will be discussed in Section 7-2.

The old system of naming molecular compounds is based on the use of prefixes. For example, the molecular compound CCl_4 is named carbon *tetra*chloride. The prefix *tetra-* indicates that four chloride atoms are present in a single molecule of the compound. The two oxides of carbon, CO and CO_2, are named carbon *mon*oxide and carbon *di*oxide, respectively.

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TABLE 7-3 Numerical Prefixes

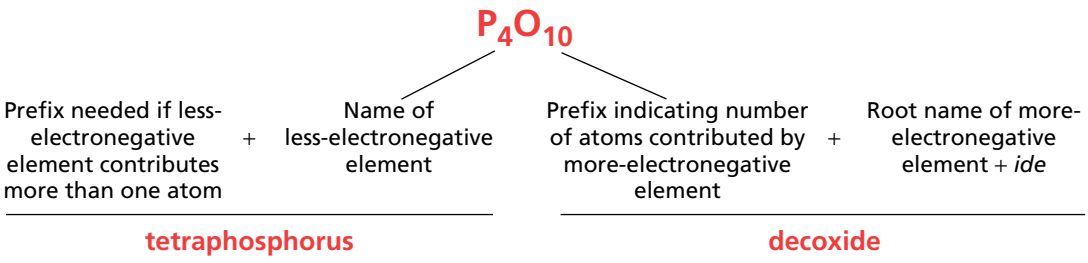
Number	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

In these names the prefix *mon-* indicates one oxygen atom and the prefix *di-* indicates two oxygen atoms. The prefixes used to specify the number of atoms, or sometimes the number of *groups* of atoms, in a molecule are listed in Table 7-3.

The rules for the prefix system of nomenclature of binary molecular compounds are as follows.

1. The less-electronegative element is given first. It is given a prefix only if it contributes more than one atom to a molecule of the compound.
2. The second element is named by combining (a) a prefix indicating the number of atoms contributed by the element, (b) the root of the name of the second element, and (c) the ending *-ide*. With few exceptions, the ending *-ide* indicates that a compound contains only two elements.
3. The *o* or *a* at the end of a prefix is usually dropped when the word following the prefix begins with another vowel, e.g., monoxide or pentoxide.

The prefix system is illustrated below.



Because the less-electronegative element is written first, oxygen and the halogens are usually given second, as in carbon tetrachloride and the carbon oxides. In general, the order of nonmetals in binary compound names and formulas is C, P, N, H, S, I, Br, Cl, O, F.

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TABLE 7-4 Binary Compounds of Nitrogen and Oxygen

Formula	Prefix-system name
N_2O	dinitrogen monoxide
NO	nitrogen monoxide
NO_2	nitrogen dioxide
N_2O_3	dinitrogen trioxide
N_2O_4	dinitrogen tetroxide
N_2O_5	dinitrogen pentoxide

The prefix system is illustrated further in Table 7-4, which lists the names of the six oxides of nitrogen. Note the application of rule 1, for example, in the name *nitrogen dioxide* for NO_2. No prefix is needed with *nitrogen* because only one atom of nitrogen, the less-electronegative element, is present in a molecule of NO_2. On the other hand, the prefix *di-* in *dioxide* is needed according to rule 2 to indicate the presence of two atoms of the more-electronegative element, oxygen. Take a moment to review the prefixes in the other names in Table 7-4.

SAMPLE PROBLEM 7-4

a. Give the name for As_2O_5.
b. Write the formula for oxygen difluoride.

SOLUTION

a. A molecule of the compound contains two arsenic atoms, so the first word in the name is "*di*arsenic." The five oxygen atoms are indicated by adding the prefix *pent-* to the word "oxide." The complete name is diarsenic pentoxide.

b. The first symbol in the formula is that for oxygen. Oxygen is first in the name because it is less electronegative than fluorine. Since there is no prefix, there must be only one oxygen atom. The prefix *di-* in *difluoride* shows that there are two fluorine atoms in the molecule. The formula is OF_2.

PRACTICE

1. Name the following binary molecular compounds:
   a. SO_3
   b. ICl_3
   c. PBr_5

2. Write formulas for the following compounds:
   a. carbon tetraiodide
   b. phosphorus trichloride
   c. dinitrogen trioxide

Answer

1. a. sulfur trioxide
   b. iodine trichloride
   c. phosphorus pentabromide

2. a. CI_4
   b. PCl_3
   c. N_2O_3

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Covalent-Network Compounds

As you read in Chapter 6, some covalent compounds do not consist of individual molecules. Instead, each atom is joined to all its neighbors in a covalently bonded, three-dimensional network. There are no distinct units in these compounds, just as there are no such units in ionic compounds. The subscripts in a formula for a covalent-network compound indicate the smallest whole-number ratio of the atoms in the compound. Naming such compounds is similar to naming molecular compounds. Some common examples are given below.

SiC	SiO_2	Si_3N_4
silicon carbide	silicon dioxide	trisilicon tetranitride

Acids and Salts

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An *acid* is a distinct type of molecular compound about which you will read much more in Chapter 15. Most acids used in the laboratory can be classified as either binary acids or oxyacids. *Binary acids* are acids that consist of two elements, usually hydrogen and one of the halogens—fluorine, chlorine, bromine, iodine. *Oxyacids* are acids that contain hydrogen, oxygen, and a third element (usually a nonmetal).

Acids were first recognized as a specific class of compounds based on their properties in solutions of water. Consequently, in chemical nomenclature, the term *acid* usually refers to a solution in water of one of these special compounds rather than to the compound itself. For example, *hydrochloric acid* refers to a water solution of the molecular compound hydrogen chloride, HCl. Some common binary and oxyacids are listed in Table 7-5.

Many polyatomic ions are produced by the loss of hydrogen ions from oxyacids. A few examples of the relationship between oxyacids and oxyanions are shown below.

sulfuric acid	H_2SO_4	sulfate	SO_4^{2-}
nitric acid	HNO_3	nitrate	NO_3^-
phosphoric acid	H_3PO_4	phosphate	PO_4^{3-}

TABLE 7-5 *Common Binary Acids and Oxyacids*

HF	hydrofluoric acid	HNO_2	nitrous acid	HClO	hypochlorous acid
HCl	hydrochloric acid	HNO_3	nitric acid	$HClO_2$	chlorous acid
HBr	hydrobromic acid	H_2SO_3	sulfurous acid	$HClO_3$	chloric acid
HI	hydriodic acid	H_2SO_4	sulfuric acid	$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid	CH_3COOH	acetic acid	H_2CO_3	carbonic acid

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FIGURE 7-2 Some common laboratory acids. Acids should always be handled with care and according to instructions. They can burn the skin, and they burn holes in clothing.

An ionic compound composed of a cation and the anion from an acid is often referred to as a **salt.** Table salt, NaCl, contains the anion from hydrochloric acid. Calcium sulfate, $CaSO_4$, is a salt containing an anion from sulfuric acid. Some salts contain anions in which one or more hydrogen atoms from the acid are retained. Such anions are named by adding the word *hydrogen* or the prefix *bi-* to the anion name. The best known such anion comes from carbonic acid, H_2CO_3.

HCO_3^-
hydrogen carbonate ion
bicarbonate ion

SECTION REVIEW

1. What is the significance of a chemical formula?
2. Write formulas for the compounds formed between the following:
   a. aluminum and bromine
   b. sodium and oxygen
   c. magnesium and iodine
   d. Pb^{2+} and O^{2-}
   e. Sn^{2+} and I^-
   f. Fe^{3+} and S^{2-}
   g. Cu^{2+} and NO_3^-
   h. NH_4^+ and SO_4^{2-}
3. Name the following compounds using the Stock system:
   a. NaI
   b. MgS
   c. CaO
   d. K_2S
   e. CuBr
   f. $FeCl_2$
4. Write formulas for each of the following compounds:
   a. barium sulfide
   b. sodium hydroxide
   c. lead(II) nitrate
   d. potassium permanganate
   e. iron(II) sulfate
   f. diphosphorus trioxide
   g. disulfur dichloride
   h. carbon diselenide
   i. acetic acid
   j. chloric acid
   k. sulfurous acid
   l. phosphoric acid

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SECTION 7-2

Oxidation Numbers

Objectives

- List the rules for assigning oxidation numbers.
- Give the oxidation number for each element in the formula of a chemical compound.
- Name binary molecular compounds using oxidation numbers and the Stock system.

The charges on the ions composing an ionic compound reflect the electron distribution of the compound. *In order to indicate the general distribution of electrons among the bonded atoms in a molecular compound or a polyatomic ion,* **oxidation numbers,** *also called* **oxidation states,** *are assigned to the atoms composing the compound or ion.* Unlike ionic charges, oxidation numbers do not have an exact physical meaning. In fact, in some cases they are quite arbitrary. However, oxidation numbers are useful in naming compounds, in writing formulas, and in balancing chemical equations. And, as will be discussed in Chapter 19, they are helpful in studying certain types of chemical reactions.

Assigning Oxidation Numbers

As a general rule in assigning oxidation numbers, shared electrons are assumed to belong to the more-electronegative atom in each bond. More specific rules for determining oxidation numbers are provided by the following guidelines.

1. The atoms in a pure element have an oxidation number of zero. For example, the atoms in pure sodium, Na, oxygen, O_2, phosphorus, P_4, and sulfur, S_8, all have oxidation numbers of zero.
2. The more-electronegative element in a binary molecular compound is assigned the number equal to the negative charge it would have as an anion. The less-electronegative atom is assigned the number equal to the positive charge it would have as a cation.
3. Fluorine has an oxidation number of –1 in all of its compounds because it is the most electronegative element.
4. Oxygen has an oxidation number of –2 in almost all compounds. Exceptions include when it is in peroxides, such as H_2O_2, in which its oxidation number is –1, and when it is in compounds with halogens, such as OF_2, in which its oxidation number is +2.
5. Hydrogen has an oxidation number of +1 in all compounds containing elements that are more-electronegative than it; it has an oxidation number of –1 in compounds with metals.
6. The algebraic sum of the oxidation numbers of all atoms in a neutral compound is equal to zero.
7. The algebraic sum of the oxidation numbers of all atoms in a polyatomic ion is equal to the charge of the ion.
8. Although rules 1 through 7 apply to covalently bonded atoms, oxidation numbers can also be assigned to atoms in ionic compounds.

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A monatomic ion has an oxidation number equal to the charge of the ion. For example, the ions Na^+, Ca^{2+}, and Cl^- have oxidation numbers of +1, +2, and –1, respectively.

Let's examine the assignment of oxidation numbers to the atoms in two molecular compounds, hydrogen fluoride, HF, and water, H_2O. In HF the bond is polar, with a partial negative charge on the fluorine atom and a partial positive charge on the hydrogen atom. If HF were an ionic compound in which an electron was fully transferred to the fluorine atom, H would have a 1+ charge and F would have a 1– charge. Thus, the oxidation numbers of H and F in hydrogen fluoride are +1 and –1, respectively. In a water molecule, the oxygen atom is more electronegative than the hydrogen atoms. If H_2O were an ionic compound, the oxygen atom would have a charge of 2– and the hydrogen atoms would each have a charge of 1+. The oxidation numbers of H and O in water are therefore +1 and –2, respectively.

Because the sum of the oxidation numbers of the atoms in a compound must satisfy rule 6 or 7 of the guidelines on page 216, it is often possible to assign oxidation numbers when they are not known. This is illustrated in Sample Problem 7-5.

SAMPLE PROBLEM 7-5

Assign oxidation numbers to each atom in the following compounds or ions:

a. UF_6

b. H_2SO_4

c. ClO_3^-

SOLUTION

a. Start by placing known oxidation numbers above the appropriate elements. From the guidelines, we know that fluorine always has an oxidation number of –1.

$$\overset{-1}{UF_6}$$

Multiply known oxidation numbers by the appropriate number of atoms and place the totals underneath the corresponding elements. There are six fluorine atoms, $6 \times -1 = -6$.

$$\begin{matrix}\overset{-1}{UF_6}\\ -6\end{matrix}$$

The compound UF_6 is molecular. According to the guidelines, the sum of the oxidation numbers must equal zero. The total of positive oxidation numbers is therefore +6.

$$\begin{matrix}\overset{-1}{UF_6}\\ +6\ -6\end{matrix}$$

Divide the total calculated oxidation number by the appropriate number of atoms. There is only one uranium atom in the molecule, so it must have an oxidation number of +6.

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$$\overset{+6\ -1}{UF_6}$$
$$\overset{+6\ -6}{}$$

b. Oxygen and sulfur are each more electronegative than hydrogen, so hydrogen has an oxidation number of +1. Oxygen is not combined with a halogen, nor is H_2SO_4 a peroxide. Therefore, the oxidation number of oxygen is –2. Place these known oxidation numbers above the appropriate symbols. Place the total of the oxidation numbers underneath.

$$\overset{+1\ \ -2}{H_2SO_4}$$
$$\overset{+2\ \ -8}{}$$

The sum of the oxidation numbers must equal zero, and there is only one sulfur atom in each molecule of H_2SO_4. Each sulfur atom therefore must have an oxidation number of (+2) + (–8) = +6.

c. To assign oxidation numbers to the elements in ClO_3^-, proceed as in parts (a) and (b). Remember, however, that the total of the oxidation numbers should equal the overall charge of the anion, 1–. The oxidation number of a single oxygen atom in the ion is –2. The total oxidation number due to the three oxygen atoms is –6. For the chlorate ion to have a 1– charge, chlorine must be assigned an oxidation number of +5.

$$\overset{+5\ -2}{ClO_3^-}$$
$$\overset{+5\ -6}{}$$

PRACTICE

1. Assign oxidation numbers to each atom in the following compounds or ions:

a. HCl
b. CF_4
c. PCl_3
d. SO_2
e. HNO_3
f. KH
g. P_4O_{10}
h. $HClO_3$
i. N_2O_5
j. $GeCl_2$

Answer

a. +1, –1
b. +4, –1
c. +3, –1
d. +4, –2
e. +1, +5, –2
f. +1, –1
g. +5, –2
h. +1, +5, –2
i. +5, –2
j. +2, –1

Using Oxidation Numbers for Formulas and Names

As shown in Table 7-6, many nonmetals can have more than one oxidation number. (A more extensive list of oxidation numbers is given in Appendix Table A-15.) These numbers can sometimes be used in the same manner as ionic charges to determine formulas. Suppose, for example, you want to know the formula of a binary compound formed between sulfur and oxygen. From the common +4 and +6 oxidation states of sulfur, you could expect that sulfur might form SO_2 or SO_3. Both are known compounds. Of course, a formula must represent facts. Oxidation numbers alone cannot be used to predict the existence of a compound.

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TABLE 7-6 Common Oxidation Numbers of Some Nonmetals That Have Variable Oxidation States*

Group 14	carbon	–4, +2, +4
Group 15	nitrogen	–3, +3, +5
	phosphorus	–3, +3, +5
Group 16	sulfur	–2, +4, +6
Group 17	chlorine	–1, +1, +3, +5, +7
	bromine	–1, +1, +3, +5, +7
	iodine	–1, +1, +3, +5, +7

*In addition to the values shown, atoms of each element in its pure state are assigned an oxidation number of zero.

In Section 7-1 we introduced the use of Roman numerals to denote ionic charges in the Stock system of naming ionic compounds. The Stock system is actually based on oxidation numbers, and it can be used as an alternative to the prefix system for naming binary molecular compounds. In the prefix system, for example, SO_2 and SO_3 are named sulfur dioxide and sulfur trioxide, respectively. Their names according to the Stock system are sulfur(IV) oxide and sulfur(VI) oxide. The international body that governs nomenclature has endorsed the Stock system, which is more practical for complicated compounds. Prefix-based names and Stock-system names are still used interchangeably for many simple compounds, however. A few additional examples of names in both systems are given below.

	Prefix system	Stock system
PCl_3	phosphorus trichloride	phosphorus(III) chloride
PCl_5	phosphorus pentachloride	phosphorus(V) chloride
N_2O	dinitrogen monoxide	nitrogen(I) oxide
NO	nitrogen monoxide	nitrogen(II) oxide
PbO_2	lead dioxide	lead(IV) oxide
Mo_2O_3	dimolybdenum trioxide	molybdenum(III) oxide

SECTION REVIEW

1. Assign oxidation numbers to each atom in the following compounds or ions:

a. HF
b. Cl_4
c. H_2O
d. PI_3
e. CS_2
f. Na_2O_2
g. H_2CO_3
h. NO_2^-
i. SO_4^{2-}
j. ClO_2^-
k. IO_3^-

2. Name each of the following binary molecular compounds according to the Stock system:

a. Cl_4
b. SO_3
c. As_2S_3
d. NCl_3

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CHEMICAL COMMENTARY

Chemistry and Art

From "Chemistry and the Plastic and Graphic Arts" by Jonathan E. Ericson
in *The Central Science, Essays on the Uses of Chemistry*

The preservation of art is dependent on the control of the environment of the piece. Modern museums are air conditioned, maintaining their temperature between 68°–72°F and a 50–65% relative humidity. These controls provide the conditions under which most works of art are stable. Occasionally, the relative humidity will have to be increased or decreased depending on the stability of an individual piece. Here, art conservation has borrowed techniques from physical chemistry to determine proper conditions experimentally.

The lighting of a work of art is also a critical part of its environment. Fluorescent light and sunlight contain a lot of ultraviolet. The exposure of art to this light can cause it to fade tremendously. Papers, textiles, and organic dyes are the most sensitive to ultraviolet fading. Here, the polymer research chemist has developed special acrylic plastics like Plexiglas® UF-3, a Rohm and Haas product, which filters out the ultraviolet light.

The relative humidity, temperature and lighting are rather easy to control in a large museum. However, the agents of attack which deteriorate the appearance of the art piece are now not always so easily identified. For paintings, the accumulation of dirt and grime, discoloring of the protective varnish layer, or the tension and distortion of canvas or wood supports are destructive to the piece and distorting to us when viewing it. In the past, when cleaning a painting, people either used stronger cleaning methods like sandpaper, or, if smart, gave up. Modern chemistry has developed ways and means of using whole families of safer cleaning agents like acetone, alcohol and other organic solvents. After careful examination and evaluation, the painting conservator can remove the old varnish, reline or bond a new supporting canvas with natural wax resin or synthetic resin, spray on an isolating layer of synthetic resin, paint in pigment losses, and seal the painting with a final protective layer. All these steps use products which have been developed in the chemical laboratory.

In many museums, the temperature and relative humidity of the surroundings are recorded on the same graph by a hygrothermograph, *as shown here.*

Finally, the agents of attack are not always so subtle. Sometimes works of art fall and break, or are torn, cut, or burned. For each case and for each object, a particular conservation method is used. Almost always, the products used or the treatment itself are direct contributions of a chemist. Without chemistry, art conservation, as we know it, would be very primitive, indeed.

Reading for Meaning

What kind of molecules are acrylic plastics composed of?

Read Further

When light interacts with paper, it can cause a *photochemical reaction.* Research photochemical reactions, and explain why a newspaper left in the sunlight for a long period of time turns yellow.

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Using Chemical Formulas

SECTION 7-3

OBJECTIVES

- Calculate the formula mass or molar mass of any given compound.
- Use molar mass to convert between mass in grams and amount in moles of a chemical compound.
- Calculate the number of molecules, formula units, or ions in a given molar amount of a chemical compound.
- Calculate the percentage composition of a given chemical compound.

As you have seen, a chemical formula indicates the elements as well as the relative number of atoms or ions of each element present in a compound. Chemical formulas also allow chemists to calculate a number of characteristic values for a given compound. In this section, you will learn how to use chemical formulas to calculate the *formula mass,* the *molar mass,* and the *percentage composition* by mass of a compound.

Formula Masses

In Chapter 3 we saw that hydrogen atoms have an average atomic mass of 1.007 94 amu and that oxygen atoms have an average atomic mass of 15.9994 amu. Like individual atoms, a molecule, a formula unit, or an ion has a characteristic average mass. For example, we know from the chemical formula H_2O that a single water molecule is composed of exactly two hydrogen atoms and one oxygen atom. The mass of a water molecule is found by summing the masses of the three atoms in the molecule. (In the calculation, the average atomic masses have been rounded to two decimal places.)

average atomic mass of H: 1.01 amu
average atomic mass of O: 16.00 amu

$$2\ \cancel{\text{H atoms}} \times \frac{1.01\ \text{amu}}{\cancel{\text{H atom}}} = 2.02\ \text{amu}$$

$$1\ \cancel{\text{O atom}} \times \frac{16.00\ \text{amu}}{\cancel{\text{O atom}}} = 16.00\ \text{amu}$$

average mass of H_2O molecule = 18.02 amu

The mass of a water molecule can be correctly referred to as a *molecular mass*. The mass of one NaCl formula unit, on the other hand, is not a molecular mass because NaCl is an ionic compound. The mass of *any* unit represented by a chemical formula, whether the unit is a molecule, a formula unit, or an ion, is known as the formula mass. *The* **formula mass** *of any molecule, formula unit, or ion is the sum of the average atomic masses of all the atoms represented in its formula.*

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The procedure illustrated for calculating the formula mass of a water molecule can be used to calculate the mass of any unit represented by a chemical formula. In each of the problems that follow, the atomic masses from the periodic table on pages 130–131 have been rounded to two decimal places.

SAMPLE PROBLEM 7-6

Find the formula mass of potassium chlorate, $KClO_3$.

SOLUTION

The mass of a formula unit of $KClO_3$ is found by summing the masses of one K atom, one Cl atom, and three O atoms. The required atomic masses can be found in the periodic table on pages 130–131. In the calculation, each atomic mass has been rounded to two decimal places.

$$1 \text{ K atom} \times \frac{39.10 \text{ amu}}{\text{K atom}} = 39.10 \text{ amu}$$

$$1 \text{ Cl atom} \times \frac{35.45 \text{ amu}}{\text{Cl atom}} = 35.45 \text{ amu}$$

$$3 \text{ O atoms} \times \frac{16.00 \text{ amu}}{\text{O atom}} = 48.00 \text{ amu}$$

formula mass of $KClO_3 = 122.55$ amu

PRACTICE

1. Find the formula mass of each of the following:
   a. H_2SO_4
   b. $Ca(NO_3)_2$
   c. PO_4^{3-}
   d. $MgCl_2$

Answer
a. 98.08 amu
b. 164.10 amu
c. 94.97 amu
d. 95.21 amu

Molar Masses

In Chapter 3 you learned that the molar mass of a substance is equal to the mass in grams of one mole, or approximately 6.022×10^{23} particles, of the substance. For example, the molar mass of pure calcium, Ca, is 40.08 g/mol because one mole of calcium atoms has a mass of 40.08 g.

The molar mass of a compound is calculated by summing the masses of the elements present in a mole of the molecules or formula units that make up the compound. For example, one mole of water molecules contains exactly two moles of H atoms and one mole of O atoms. Rounded to two decimal places, a mole of hydrogen atoms has a mass

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of 1.01 g, and a mole of oxygen atoms has a mass of 16.00 g. The molar mass of water is calculated as follows.

$$2 \text{ mol H} \times \frac{1.01 \text{ g H}}{\text{mol H}} = 2.02 \text{ g H}$$

$$1 \text{ mol O} \times \frac{16.00 \text{ g O}}{\text{mol O}} = 16.00 \text{ g O}$$

$$\text{molar mass of } H_2O = 18.02 \text{ g/mol}$$

Figure 7-3 shows a mole of water as well as a mole of several other substances.

You may have noticed that *a compound's molar mass is numerically equal to its formula mass*. For instance, in Sample Problem 7-6 the formula mass of $KClO_3$ was found to be 122.55 amu. Therefore, because molar mass is numerically equal to formula mass, we know that the molar mass of $KClO_3$ is 122.55 g/mol.

FIGURE 7-3 Every compound has a characteristic molar mass. Shown here are one mole each of nitrogen (in balloon), water (in graduated cylinder), cadmium sulfide, CdS (yellow substance), and sodium chloride, NaCl (white substance).

SAMPLE PROBLEM 7-7

What is the molar mass of barium nitrate, $Ba(NO_3)_2$?

SOLUTION

One mole of barium nitrate contains exactly one mole of Ba^{2+} ions and two moles of NO_3^- ions. The two moles of NO_3^- ions contain two moles of N atoms and six moles of O atoms. Therefore, the molar mass of $Ba(NO_3)_2$ is calculated as follows.

$$1 \text{ mol Ba} \times \frac{137.33 \text{ g Ba}}{\text{mol Ba}} = 137.33 \text{ g Ba}$$

$$2 \text{ mol N} \times \frac{14.01 \text{ g N}}{\text{mol N}} = 28.02 \text{ g N}$$

$$6 \text{ mol O} \times \frac{16.00 \text{ g O}}{\text{mol O}} = 96.00 \text{ g O}$$

$$\text{molar mass of } Ba(NO_3)_2 = 261.35 \text{ g/mol}$$

PRACTICE

1. How many moles of atoms of each element are there in one mole of the following compounds?
   a. Al_2S_3
   b. $NaNO_3$
   c. $Ba(OH)_2$

Answer

1. a. 2 mol Al, 3 mol S
   b. 1 mol Na, 1 mol N, 3 mol O
   c. 1 mol Ba, 2 mol O, 2 mol H

2. Find the molar mass of each of the compounds listed in item 1.

2. a. 150.17 g/mol
   b. 85.00 g/mol
   c. 171.35 g/mol

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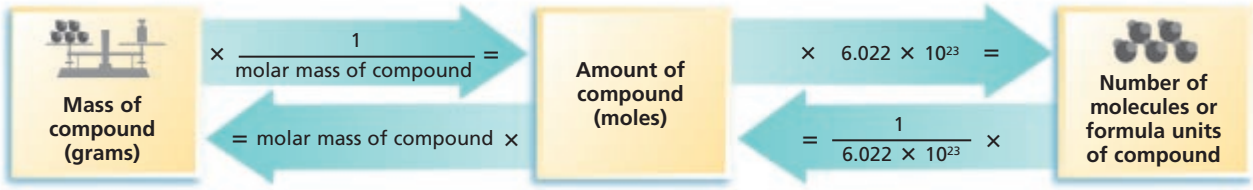
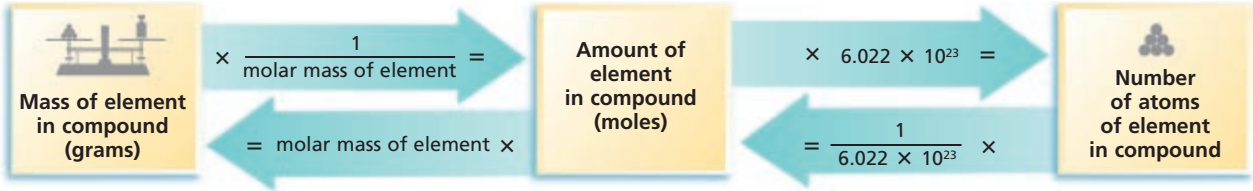

Mass of compound (grams)
× 1 / molar mass of compound =
= molar mass of compound ×
Amount of compound (moles)
× 6.022 × 10²³ =
= 1 / 6.022 × 10²³ ×
Number of molecules or formula units of compound

(a)


Mass of element in compound (grams)
× 1 / molar mass of element =
= molar mass of element ×
Amount of element in compound (moles)
× 6.022 × 10²³ =
= 1 / 6.022 × 10²³ ×
Number of atoms of element in compound

(b)

FIGURE 7-4 (a) The diagram shows the relationships between mass in grams, amount in moles, and number of molecules or atoms for a given compound. (b) Similar relationships exist for an element within a compound.

Molar Mass as a Conversion Factor

The molar mass of a compound can be used as a conversion factor to relate an amount in moles to a mass in grams for a given substance. Recall that molar mass usually has the units of grams per mole. To convert a known amount of a compound in moles to a mass in grams, multiply the amount in moles by the molar mass.

$$\text{amount in moles} \times \text{molar mass (g/mol)} = \text{mass in grams}$$

Conversions of this type for elements and compounds are summarized above in Figure 7-4.

SAMPLE PROBLEM 7-8

What is the mass in grams of 2.50 mol of oxygen gas?

SOLUTION

1 ANALYZE

Given: 2.50 mol O_2
Unknown: mass of O_2 in grams

2 PLAN

moles O_2 ⟶ grams O_2
To convert amount of O_2 in moles to mass of O_2 in grams, multiply by the molar mass of O_2.

$$\text{amount of } O_2 \text{ (mol)} \times \text{molar mass of } O_2 \text{ (g/mol)} = \text{mass of } O_2 \text{ (g)}$$

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3 COMPUTE First the molar mass of O_2 must be calculated.

$$2 \text{ mol O} \times \frac{16.00 \text{ g O}}{\text{mol O}} = 32.00 \text{ g (mass of one mole of } O_2)$$

The molar mass of O_2 is therefore 32.00 g/mol. Now do the calculation shown in step 2.

$$2.50 \text{ mol } O_2 \times \frac{32.00 \text{ g } O_2}{\text{mol } O_2} = 80.0 \text{ g } O_2$$

4 EVALUATE The answer is correctly given to three significant figures and is close to an estimated value of 75 g (2.50 mol × 30 g/mol).

To convert a known mass of a compound in grams to an amount in moles, the mass must be divided by the molar mass. Or you can invert the molar mass and multiply so that units are easily canceled.

$$\text{mass in grams} \times \frac{1}{\text{molar mass (g/mol)}} = \text{amount in moles}$$

SAMPLE PROBLEM 7-9

Ibuprofen, $C_{13}H_{18}O_2$, is the active ingredient in many nonprescription pain relievers. Its molar mass is 206.29 g/mol.

a. If the tablets in a bottle contain a total of 33 g of ibuprofen, how many moles of ibuprofen are in the bottle?

b. How many molecules of ibuprofen are in the bottle?

c. What is the total mass in grams of carbon in 33 g of ibuprofen?

SOLUTION

1 ANALYZE

Given: 33 g of $C_{13}H_{18}O_2$, molar mass 206.29 g/mol

Unknown: **a.** moles $C_{13}H_{18}O_2$
b. molecules $C_{13}H_{18}O_2$
c. total mass of C

2 PLAN

a. grams ⟶ moles

To convert mass of ibuprofen in grams to amount of ibuprofen in moles, multiply by the inverted molar mass of $C_{13}H_{18}O_2$.

$$\text{g } C_{13}H_{18}O_2 \times \frac{1 \text{ mol } C_{13}H_{18}O_2}{206.29 \text{ g } C_{13}H_{18}O_2} = \text{mol } C_{13}H_{18}O_2$$

b. moles ⟶ molecules

To find the number of molecules of ibuprofen, multiply amount of $C_{13}H_{18}O_2$ in moles by Avogadro's number.

$$\text{mol } C_{13}H_{18}O_2 \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = \text{molecules } C_{13}H_{18}O_2$$

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c. moles $C_{13}H_{18}O_2 \longrightarrow$ moles C $\longrightarrow$ grams C
To find the mass of carbon present in the ibuprofen, the two conversion factors needed are the amount of carbon in moles per mole of $C_{13}H_{18}O_2$ and the molar mass of carbon.

$$\text{mol } C_{13}H_{18}O_2 \times \frac{13 \text{ mol C}}{\text{mol } C_{13}H_{18}O_2} \times \frac{12.01 \text{ g C}}{\text{mol C}} = \text{g C}$$

3 COMPUTE

a. $33 \text{ g } C_{13}H_{18}O_2 \times \frac{1 \text{ mol } C_{13}H_{18}O_2}{206.29 \text{ g } C_{13}H_{18}O_2} = 0.16 \text{ mol } C_{13}H_{18}O_2$

b. $0.16 \text{ mol } C_{13}H_{18}O_2 \times \frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}} = 9.6 \times 10^{22} \text{ molecules } C_{13}H_{18}O_2$

c. $0.16 \text{ mol } C_{13}H_{18}O_2 \times \frac{13 \text{ mol C}}{\text{mol } C_{13}H_{18}O_2} \times \frac{12.01 \text{ g C}}{\text{mol C}} = 25 \text{ g C}$

The bottle contains 0.16 mol of ibuprofen, which is 9.6×10^{22} molecules of ibuprofen. The sample of ibuprofen contains 25 g of carbon.

4 EVALUATE

Checking each step shows that the arithmetic is correct, significant figures have been used correctly, and units have canceled as desired.

PRACTICE

1. How many moles of compound are there in the following?
   a. 6.60 g $(NH_4)_2SO_4$
   b. 4.5 kg $Ca(OH)_2$
2. How many molecules are there in the following?
   a. 25.0 g H_2SO_4
   b. 125 g of sugar, $C_{12}H_{22}O_{11}$
3. What is the mass in grams of 6.25 mol of copper(II) nitrate?

Answer

1. a. 0.0500 mol
   b. 61 mol
2. a. 1.53×10^{23} molecules
   b. 2.20×10^{23} molecules
3. 1170 g

Percentage Composition

It is often useful to know the percentage by mass of a particular element in a chemical compound. For example, suppose the compound potassium chlorate, $KClO_3$, were to be used as a source of oxygen. It would be helpful to know the percentage of oxygen in the compound. To find the mass percentage of an element in a compound, one can divide the mass of the element in a sample of the compound by the total mass of the sample, then multiply this value by 100.

$$\frac{\text{mass of element in sample of compound}}{\text{mass of sample of compound}} \times 100 = \% \text{ element in compound}$$

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The mass percentage of an element in a compound is the same regardless of the sample's size. Therefore, a simpler way to calculate the percentage of an element in a compound is to determine how many grams of the element are present in one mole of the compound. Then divide this value by the molar mass of the compound and multiply by 100.

$$\frac{\text{mass of element in 1 mol of compound}}{\text{molar mass of compound}} \times 100 = \%\ \text{element in compound}$$

The percentage by mass of each element in a compound is known as the **percentage composition** *of the compound.*

SAMPLE PROBLEM 7-10

Find the percentage composition of copper(I) sulfide, Cu_2S.

SOLUTION

1 ANALYZE

Given: formula, Cu_2S
Unknown: percentage composition of Cu_2S

2 PLAN

formula ⟶ molar mass ⟶ mass percentage of each element

The molar mass of the compound must be found. Then the mass of each element present in one mole of the compound is used to calculate the mass percentage of each element.

3 COMPUTE

$$2\ \cancel{\text{mol Cu}} \times \frac{63.55\ \text{g Cu}}{\cancel{\text{mol Cu}}} = 127.1\ \text{g Cu}$$

$$1\ \cancel{\text{mol S}} \times \frac{32.07\ \text{g S}}{\cancel{\text{mol S}}} = 32.07\ \text{g S}$$

$$\text{molar mass of } Cu_2S = 159.2\ \text{g}$$

$$\frac{127.1\ \text{g Cu}}{159.2\ \text{g } Cu_2S} \times 100 = 79.84\%\ \text{Cu}$$

$$\frac{32.07\ \text{g S}}{159.2\ \text{g } Cu_2S} \times 100 = 20.14\%\ \text{S}$$

4 EVALUATE

A good check is to see if the results add up to about 100%. (Because of rounding, the total may not always be exactly 100%.)

SAMPLE PROBLEM 7-11

As some salts crystallize from a water solution, they bind water molecules in their crystal structure. Sodium carbonate forms such a *hydrate,* in which 10 water molecules are present for every formula unit of sodium carbonate. Find the mass percentage of water in sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$, which has a molar mass of 286.14 g/mol.

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SOLUTION

1 ANALYZE

Given: chemical formula, $Na_2CO_3 \cdot 10H_2O$
molar mass of $Na_2CO_3 \cdot 10H_2O$
Unknown: mass percentage of H_2O

2 PLAN

chemical formula $\longrightarrow$ mass H_2O per mole of $Na_2CO_3 \cdot 10H_2O$ $\longrightarrow$ % water

The mass of water per mole of sodium carbonate decahydrate must first be found. This value is then divided by the mass of one mole of $Na_2CO_3 \cdot 10H_2O$.

3 COMPUTE

One mole of $Na_2CO_3 \cdot 10H_2O$ contains 10 mol of H_2O. Recall from page 223 that the molar mass of H_2O is 18.02 g/mol. The mass of 10 mol of H_2O is calculated as follows.

$$10 \text{ mol } H_2O \times \frac{18.02 \text{ g } H_2O}{\text{mol } H_2O} = 180.2 \text{ g } H_2O$$

$$\text{mass of } H_2O \text{ per mole of } Na_2CO_3 \cdot 10H_2O = 180.2 \text{ g}$$

The molar mass of $Na_2CO_3 \cdot 10H_2O$ is 286.14 g/mol, so we know that 1 mol of the hydrate has a mass of 286.14g. The mass percentage of 10 mol of H_2O in 1 mol of $Na_2CO_3 \cdot 10H_2O$ can now be calculated.

$$\text{mass percentage of } H_2O \text{ in } Na_2CO_3 \cdot 10H_2O = \frac{180.2 \text{ g } H_2O}{286.14 \text{ g } Na_2CO_3 \cdot 10H_2O} \times 100 = 62.98\% \text{ } H_2O$$

4 EVALUATE

Checking shows that the arithmetic is correct and that units cancel as desired.

PRACTICE

1. Find the percentage compositions of the following:
   a. $PbCl_2$ b. $Ba(NO_3)_2$
2. Find the mass percentage of water in $ZnSO_4 \cdot 7H_2O$.
3. Magnesium hydroxide is 54.87% oxygen by mass. How many grams of oxygen are in 175 g of the compound? How many moles of oxygen is this?

Answer

1. a. 74.51% Pb, 25.49% Cl
   b. 52.55% Ba, 10.72% N, 36.73% O
2. 43.86% H_2O
3. 96.0 g O; 6.00 mol O

SECTION REVIEW

1. Determine both the formula mass and molar mass of ammonium carbonate, $(NH_4)_2CO_3$.
2. How many moles of atoms of each element are there in one mole of $(NH_4)_2CO_3$?
3. What is the mass in grams of 3.25 mol $Fe_2(SO_4)_3$?
4. How many moles of molecules are there in 250 g of hydrogen nitrate, HNO_3?
5. How many molecules of aspirin, $C_9H_8O_4$, are there in a 100.0 mg tablet of aspirin?
6. Calculate the percentage composition of $(NH_4)_2CO_3$.

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SECTION 7-4

Determining Chemical Formulas

OBJECTIVES

- Define *empirical formula,* and explain how the term applies to ionic and molecular compounds.
- Determine an empirical formula from either a percentage or a mass composition.
- Explain the relationship between the empirical formula and the molecular formula of a given compound.
- Determine a molecular formula from an empirical formula.

When a new substance is synthesized or is discovered, it is analyzed quantitatively to reveal its percentage composition. From this data, the empirical formula is then determined. *An* **empirical formula** *consists of the symbols for the elements combined in a compound, with subscripts showing the smallest whole-number mole ratio of the different atoms in the compound.* For an ionic compound, the formula unit is usually the compound's empirical formula. For a molecular compound, however, the empirical formula does not necessarily indicate the actual numbers of atoms present in each molecule. For example, the empirical formula of the gas diborane is BH_3, but the molecular formula is B_2H_6. In this case, the number of atoms given by the molecular formula corresponds to the empirical ratio multiplied by two.

Calculation of Empirical Formulas

To determine a compound's empirical formula from its percentage composition, begin by converting percentage composition to a mass composition. Assume that you have a 100.0 g sample of the compound. Then calculate the amount of each element in the sample. For example, the percentage composition of diborane is 78.1% B and 21.9% H. Therefore, 100.0 g of diborane contains 78.1 g of B and 21.9 g of H.

Next, the mass composition of each element is converted to a composition in moles by dividing by the appropriate molar mass.

$$78.1 \text{ g B} \times \frac{1 \text{ mol B}}{10.81 \text{ g B}} = 7.22 \text{ mol B}$$

$$21.9 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 21.7 \text{ mol H}$$

These values give a mole ratio of 7.22 mol B to 21.7 mol H. However, this is not a ratio of smallest whole numbers. To find such a ratio, divide each number of moles by the smallest number in the existing ratio.

$$\frac{7.22 \text{ mol B}}{7.22} : \frac{21.7 \text{ mol H}}{7.22} = 1 \text{ mol B}:3.01 \text{ mol H}$$

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Because of rounding or experimental error, a compound's mole ratio sometimes consists of numbers close to whole numbers instead of exact whole numbers. In this case, the differences from whole numbers may be ignored and the nearest whole number taken. Thus, diborane contains atoms in the ratio 1 B:3 H. The compound's empirical formula is BH_3.

Sometimes mass composition is known instead of percentage composition. To determine the empirical formula in this case, convert mass composition to composition in moles. Then calculate the smallest whole-number mole ratio of atoms. This process is shown in Sample Problem 7-13.

SAMPLE PROBLEM 7-12

Quantitative analysis shows that a compound contains 32.38% sodium, 22.65% sulfur, and 44.99% oxygen. Find the empirical formula of this compound.

SOLUTION

1 ANALYZE

Given: percentage composition: 32.38% Na, 22.65% S, and 44.99% O
Unknown: empirical formula

2 PLAN

percentage composition $\longrightarrow$ mass composition $\longrightarrow$ composition in moles $\longrightarrow$ smallest whole-number mole ratio of atoms

3 COMPUTE

Mass composition (mass of each element in 100.0 g sample): 32.38 g Na, 22.65 g S, 44.99 g O

Composition in moles:

$$32.38 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 1.408 \text{ mol Na}$$

$$22.65 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 0.7063 \text{ mol S}$$

$$44.99 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.812 \text{ mol O}$$

Smallest whole-number mole ratio of atoms:
The compound contains atoms in the ratio 1.408 mol Na:0.7063 mol S:2.812 mol O. To find the smallest whole-number mole ratio, divide each value by the smallest number in the ratio.

$$\frac{1.408 \text{ mol Na}}{0.7063} : \frac{0.7063 \text{ mol S}}{0.7063} : \frac{2.812 \text{ mol O}}{0.7063} = 1.993 \text{ mol Na}:1 \text{ mol S}:3.981 \text{ mol O}$$

Rounding each number in the ratio to the nearest whole number yields a mole ratio of 2 mol Na:1 mol S:4 mol O. The empirical formula of the compound is Na_2SO_4.

4 EVALUATE

Calculating the percentage composition of the compound based on the empirical formula determined in the problem reveals a percentage composition of 32.37% Na, 22.58% S, and 45.05% O. These values agree reasonably well with the given percentage composition.

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SAMPLE PROBLEM 7-13

Analysis of a 10.150 g sample of a compound known to contain only phosphorus and oxygen indicates a phosphorus content of 4.433 g. What is the empirical formula of this compound?

SOLUTION

1 ANALYZE

Given: sample mass = 10.150 g
phosphorus mass = 4.433 g
Unknown: empirical formula

2 PLAN

Mass composition ⟶ composition in moles ⟶ smallest whole-number ratio of atoms

3 COMPUTE

The mass of oxygen is found by subtracting the phosphorus mass from the sample mass.

$$\text{sample mass} - \text{phosphorus mass} = 10.150\ \text{g} - 4.433\ \text{g} = 5.717\ \text{g}$$

Mass composition: 4.433 g P, 5.717 g O

Composition in moles:

$$4.433\ \text{g P} \times \frac{1\ \text{mol P}}{30.97\ \text{g P}} = 0.1431\ \text{mol P}$$

$$5.717\ \text{g O} \times \frac{1\ \text{mol O}}{16.00\ \text{g O}} = 0.3573\ \text{mol O}$$

Smallest whole-number mole ratio of atoms:

$$\frac{0.1431\ \text{mol P}}{0.1431} : \frac{0.3573\ \text{mol O}}{0.1431}$$

$$1\ \text{mol P} : 2.497\ \text{mol O}$$

The number of O atoms is not close to a whole number. But if we multiply each number in the ratio by 2, then the number of O atoms becomes 4.994 mol, which is close to 5 mol. The simplest whole-number mole ratio of P atoms to O atoms is 2:5. The compound's empirical formula is P_2O_5.

4 EVALUATE

The arithmetic is correct, significant figures have been used correctly, and units cancel as desired. The formula is reasonable because +5 is a common oxidation state of phosphorus.

PRACTICE

1. A compound is found to contain 63.52% iron and 36.48% sulfur. Find its empirical formula. *Answer* FeS
2. Find the empirical formula of a compound found to contain 26.56% potassium, 35.41% chromium, and the remainder oxygen. *Answer* $K_2Cr_2O_7$
3. Analysis of 20.0 g of a compound containing only calcium and bromine indicates that 4.00 g of calcium are present. What is the empirical formula of the compound formed? *Answer* $CaBr_2$

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Calculation of Molecular Formulas

Remember that the *empirical formula* contains the smallest possible whole numbers that describe the atomic ratio. The *molecular formula* is the actual formula of a molecular compound. An empirical formula may or may not be a correct molecular formula. For example, diborane's empirical formula is BH_3. Any multiple of BH_3, such as B_2H_6, B_3H_9, B_4H_{12}, and so on, represents the same ratio of B atoms to H atoms. The molecular compounds ethene, C_2H_4, and cyclopropane, C_3H_6, also share an identical atomic ratio (2 H:1 C), yet they are very different substances. How is the correct formula of a molecular compound found from an empirical formula?

The relationship between a compound's empirical formula and its molecular formula can be written as follows.

$$x(\text{empirical formula}) = \text{molecular formula}$$

The number represented by x is a whole-number multiple indicating the factor by which the subscripts in the empirical formula must be multiplied to obtain the molecular formula. (The value of x is sometimes 1.) The formula masses have a similar relationship.

$$x(\text{empirical formula mass}) = \text{molecular formula mass}$$

To determine the molecular formula of a compound, you must know the compound's formula mass. For example, experimentation shows the formula mass of diborane to be 27.67 amu. The formula mass for the empirical formula, BH_3, is 13.84 amu. Dividing the experimental formula mass by the empirical formula mass gives the value of x for diborane.

$$x = \frac{27.67 \text{ amu}}{13.84 \text{ amu}} = 2.000$$

The molecular formula of diborane is therefore B_2H_6.

$$(BH_3)_2 = B_2H_6$$

Recall that a compound's molecular formula mass is numerically equal to its molar mass, so a compound's molecular formula can also be found given the compound's empirical formula and its molar mass.

SAMPLE PROBLEM 7-14

In Sample Problem 7-13, the empirical formula of a compound of phosphorus and oxygen was found to be P_2O_5. Experimentation shows that the molar mass of this compound is 283.89 g/mol. What is the compound's molecular formula?

SOLUTION

1 *ANALYZE*

Given: empirical formula
Unknown: molecular formula

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2 PLAN

$$x(\text{empirical formula}) = \text{molecular formula}$$

$$x = \frac{\text{molecular formula mass}}{\text{empirical formula mass}}$$

3 COMPUTE

Molecular formula mass is numerically equal to molar mass. Thus, changing the g/mol unit of the compound's molar mass to amu yields the compound's molecular formula mass.

molecular molar mass = 283.89 g/mol
molecular formula mass = 283.89 amu

The empirical formula mass is found by adding the masses of each of the atoms indicated in the empirical formula.

mass of phosphorus atom = 30.97 amu
mass of oxygen atom = 16.00 amu
empirical formula mass of $P_2O_5 = 2 \times 30.97 \text{ amu} + 5 \times 16.00 \text{ amu} = 141.94 \text{ amu}$

Dividing the experimental formula mass by the empirical formula mass gives the value of x. The formula mass is numerically equal to the molar mass.

$$x = \frac{283.89 \cancel{\text{amu}}}{141.94 \cancel{\text{amu}}} = 2.0001$$

The compound's molecular formula is therefore P_4O_{10}.

$$2 \times (P_2O_5) = P_4O_{10}$$

4 EVALUATE

Checking the arithmetic shows that it is correct.

PRACTICE

1. Determine the molecular formula of the compound with an empirical formula of CH and a formula mass of 78.110 amu. *Answer* C_6H_6
2. A sample of a compound with a formula mass of 34.00 amu is found to consist of 0.44 g H and 6.92 g O. Find its molecular formula. *Answer* H_2O_2

SECTION REVIEW

1. A compound is found to contain 36.48% Na, 25.41% S, and 38.11% O. Find its empirical formula.
2. Find the empirical formula of a compound that contains 53.70% iron and 46.30% sulfur.
3. Analysis of a compound indicates that it contains 1.04 g K, 0.70 g Cr, and 0.86 g O. Find its empirical formula.
4. If 4.04 g of N combine with 11.46 g O to produce a compound with a formula mass of 108.0 amu, what is the molecular formula of this compound?
5. The molar mass of a compound is 92 g/mol. Analysis of a sample of the compound indicates that it contains 0.606 g N and 1.390 g O. Find its molecular formula.

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CHAPTER 7 REVIEW

CHAPTER SUMMARY

7-1

- A positive monatomic ion is identified simply by the name of the appropriate element. A negative monatomic ion is named by dropping parts of the ending of the element's name and adding *-ide* to the root.
- The charge of each ion in an ionic compound may be used to determine the simplest chemical formula for the compound.
- Compounds composed of two different elements are known as binary compounds.
- Binary ionic compounds are named by combining the names of the positive and negative ions. Compounds containing polyatomic ions are named in the same manner.
- The old system of naming binary molecular compounds uses prefixes. The new system, known as the Stock system, uses oxidation numbers.

Vocabulary

binary compounds (206) nomenclature (206) oxyanions (209) salt (215)
monatomic ions (204)

7-2

- Oxidation numbers, or oxidation states, are assigned to atoms in compounds according to a set of specific rules. Oxidation numbers are useful in naming compounds, in writing formulas, and in balancing chemical equations.
- Compounds containing elements that have more than one oxidation state are named using the Stock system of nomenclature.
- Stock-system names and prefix-system names are used interchangeably for many molecular compounds.
- In many molecular compounds, oxidation numbers of each element in the compound may be used to determine the compound's simplest chemical formula.
- By knowing oxidation numbers, we can name compounds without knowing whether they are ionic or molecular.

Vocabulary

oxidation numbers (216) oxidation states (216)

7-3

- Formula mass, molar mass, and percentage composition can be calculated from the chemical formula for a compound.
- The percentage composition of a compound is the percentage by mass of each element in the compound.
- Molar mass can be used as a conversion factor between an amount in moles and a mass in grams of a given compound or element.

Vocabulary

formula mass (221) percentage composition (227)

7-4

- An empirical formula shows the simplest whole-number ratio of atoms in a given compound.
- Each molecule of a molecular compound contains a whole-number multiple of the atoms in the empirical formula. In some cases this whole-number multiple is equal to 1.
- Empirical formulas indicate how many atoms of each element are combined in the simplest unit of a chemical compound.
- A molecular formula can be found from the empirical formula if the molar mass is measured.

Vocabulary

empirical formula (229)

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REVIEWING CONCEPTS

1. a. What are monatomic ions?
b. Give three examples of monatomic ions. (7-1)

2. What is the difference between the nitrite ion and the nitrate ion? (7-1)

3. Using only the periodic table, write the symbol of the ion most typically formed by each of the following elements:
a. K
b. Ca
c. S
d. Cl
e. Ba
f. Br (7-1)

4. Write the formulas and indicate the charges for each of the following ions:
a. sodium ion
b. aluminum ion
c. chloride ion
d. nitride ion
e. iron(II) ion
f. iron(III) ion (7-1)

5. Name each of the following monatomic ions:
a. K^+ d. Cl^-
b. Mg^{2+} e. O^{2-}
c. Al^{3+} f. Ca^{2+} (7-1)

6. Write formulas for the binary ionic compounds formed between the following elements. (Hint: See Sample Problem 7-1.)
a. sodium and iodine
b. calcium and sulfur
c. zinc and chlorine
d. barium and fluorine
e. lithium and oxygen (7-1)

7. Give the name of each of the following binary ionic compounds. (Hint: See Sample Problem 7-2.)
a. KCl c. Li_2O
b. $CaBr_2$ d. $MgCl_2$ (7-1)

8. Write the formulas and give the names of the compounds formed by the following ions:
a. Cr^{2+} and F^-
b. Ni^{2+} and O^{2-}
c. Fe^{3+} and O^{2-} (7-1)

9. In naming and writing formulas for binary molecular compounds, what determines the order in which the component elements are written? (7-1)

10. Name the following binary molecular compounds according to the prefix system. (Hint: See Sample Problem 7-4.)
a. CO_2 d. SeF_6
b. CCl_4 e. As_2O_5
c. PCl_5 (7-1)

11. Write formulas for each of the following binary molecular compounds. (Hint: See Sample Problem 7-4.)
a. carbon tetrabromide
b. silicon dioxide
c. tetraphosphorus decoxide
d. diarsenic trisulfide (7-1)

12. Distinguish between binary acids and oxyacids, and give two examples of each. (7-1)

13. a. What is a salt?
b. Give two examples of salts. (7-1)

14. Name each of the following acids:
a. HF d. H_2SO_4
b. HBr e. H_3PO_4
c. HNO_3 (7-1)

15. Give the molecular formula of each of the following acids:
a. sulfurous acid
b. chloric acid
c. hydrochloric acid
d. hypochlorous acid
e. perchloric acid
f. carbonic acid
g. acetic acid (7-3)

16. Name each of the following ions according to the Stock system:
a. Fe^{2+} d. Pb^{4+}
b. Fe^{3+} e. Sn^{2+}
c. Pb^{2+} f. Sn^{4+} (7-2)

17. Name each of the binary molecular compounds in item 11 using the Stock system. (7-2)

18. Write formulas for each of the following compounds:
a. phosphorus(III) iodide
b. sulfur(II) chloride
c. carbon(IV) sulfide
d. nitrogen(V) oxide (7-2)

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19. a. What are oxidation numbers?
b. What useful functions do oxidation numbers serve? (7-2)

20. a. Define *formula mass*.
b. In what unit is formula mass expressed? (7-3)

21. What is meant by the molar mass of a compound? (7-3)

22. What three types of information are needed in order to find an empirical formula from percentage composition data? (7-4)

23. What is the relationship between the empirical formula and the molecular formula of a compound? (7-4)

PROBLEMS

Nomenclature and Chemical Formulas

24. Write the formula and charge for each of the following ions:
a. ammonium ion
b. acetate ion
c. hydroxide ion
d. carbonate ion
e. sulfate ion
f. phosphate ion
g. copper(II) ion
h. tin(II) ion
i. iron(III) ion
j. copper(I) ion
k. mercury(I) ion
l. mercury(II) ion

25. Name each of the following ions:
a. NH_4^+
b. ClO_3^-
c. OH^-
d. SO_4^{2-}
e. NO_3^-
f. CO_3^{2-}
g. PO_4^{3-}
h. CH_3COO^-
i. HCO_3^-
j. CrO_4^{2-}

26. Write formulas for each of the following compounds:
a. sodium fluoride
b. calcium oxide
c. potassium sulfide
d. magnesium chloride
e. aluminum bromide
f. lithium nitride
g. iron(II) oxide

Oxidation Number and Stock System

27. Name each of the following ionic compounds using the Stock system:
a. NaCl
b. KF
c. CaS
d. $Co(NO_3)_2$
e. $FePO_4$
f. Hg_2SO_4
g. $Hg_3(PO_4)_2$

28. Assign oxidation numbers to each atom in the following compounds. (Hint: See Sample Problem 7-5.)
a. HI
b. PBr_3
c. GeS_2
d. KH
e. As_2O_5
f. H_3PO_4

29. Assign oxidation numbers to each atom in the following ions. (Hint: See Sample Problem 7-5.)
a. NO_3^-
b. ClO_4^-
c. PO_4^{3-}
d. $Cr_2O_7^{2-}$
e. CO_3^{2-}

Mole Relationships and Percentage Composition

30. Determine the formula mass of each of the following compounds or ions. (Hint: See Sample Problem 7-6.)
a. glucose, $C_6H_{12}O_6$
b. calcium acetate, $Ca(CH_3COO)_2$
c. the ammonium ion, NH_4^+
d. the chlorate ion, ClO_3^-

31. Determine the number of moles of each type of monatomic or polyatomic ion in one mole of the following compounds. For each polyatomic ion, determine the number of moles of each atom present in one mole of the ion.
a. KNO_3
b. Na_2SO_4
c. $Ca(OH)_2$
d. $(NH_4)_2SO_3$
e. $Ca_3(PO_4)_2$
f. $Al_2(CrO_4)_3$

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32. Determine the molar mass of each compound listed in item 31. (Hint: See Sample Problem 7-7.)

33. Determine the number of moles of compound in each of the following samples. (Hint: See Sample Problem 7-9.)
a. 4.50 g H_2O
b. 471.6 g $Ba(OH)_2$
c. 129.68 g $Fe_3(PO_4)_2$

34. Determine the percentage composition of each of the following compounds. (Hint: See Sample Problem 7-10.)
a. NaCl
b. $AgNO_3$
c. $Mg(OH)_2$

35. Determine the percentage by mass of water in the hydrate $CuSO_4 \cdot 5H_2O$. (Hint: See Sample Problem 7-11.)

36. Determine the empirical formula of a compound containing 63.50% silver, 8.25% nitrogen, and the remainder oxygen. (Hint: See Sample Problem 7-12.)

37. Determine the empirical formula of a compound found to contain 52.11% carbon, 13.14% hydrogen, and 34.75% oxygen.

38. What is the molecular formula of the molecule that has an empirical formula of CH_2O and a molar mass of 120.12 g/mol?

39. A compound with a formula mass of 42.08 amu is found to be 85.64% carbon and 14.36% hydrogen by mass. Find its molecular formula.

MIXED REVIEW

40. Chemical analysis of citric acid shows that it contains 37.51% C, 4.20% H, and 58.29% O. What is its empirical formula?

41. Name each of the following compounds using the Stock system:
a. LiBr
b. $Sn(NO_3)_2$
c. $FeCl_2$
d. MgO
e. KOH
f. Fe_2O_3
g. $AgNO_3$
h. $Fe(OH)_2$
i. CrF_2

42. What is the mass in grams of each of the following samples?
a. 1.000 mol NaCl
b. 2.000 mol H_2O
c. 3.500 mol $Ca(OH)_2$
d. 0.625 mol $Ba(NO_3)_2$

43. Determine the formula mass and molar mass of each of the following compounds:
a. XeF_4
b. $C_{12}H_{24}O_6$
c. Hg_2I_2
d. CuCN

44. Write the chemical formulas for the following compounds:
a. aluminum fluoride
b. magnesium oxide
c. vanadium(V) oxide
d. cobalt(II) sulfide
e. strontium bromide
f. sulfur trioxide

45. How many atoms of each element are contained in a single formula unit of iron(III) formate, $Fe(CHO_2)_3 \cdot H_2O$? What percentage by mass of the compound is water?

46. Name each of the following acids, and assign oxidation numbers to the atoms in each:
a. HNO_2
b. H_2SO_3
c. H_2CO_3
d. HI

47. Determine the percentage composition of the following compounds:
a. NaClO
b. H_2SO_3
c. C_2H_5COOH
d. $BeCl_2$

48. Name each of the following binary compounds:
a. MgI_2
b. NaF
c. CS_2
d. N_2O_4
e. SO_2
f. PBr_3
g. $CaCl_2$
h. AgI

49. Assign oxidation numbers to each atom in the following molecules and ions:
a. CO_2
b. NH_4^+
c. MnO_4^-
d. $S_2O_3^{2-}$
e. H_2O_2
f. P_4O_{10}
g. OF_2

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50. A 175.0 g sample of a compound contains 56.15 g C, 9.43 g H, 74.81 g O, 13.11 g N, and 21.49 g Na. What is its empirical formula?

CRITICAL THINKING

51. Analyzing Information Sulfur trioxide is produced in the atmosphere through a reaction of sulfur dioxide and oxygen. Sulfur dioxide is a primary air pollutant. List all of the chemical information you can by analyzing the formula for sulfur trioxide.

52. Analyzing Data In the laboratory, a sample of pure nickel was placed in a clean, dry, weighed crucible. The crucible was heated so that the nickel would react with the oxygen in the air. After the reaction appeared complete, the crucible was allowed to cool and the mass was determined. The crucible was reheated and allowed to cool. Its mass was then determined again to be certain that the reaction was complete. The following data were collected:

Mass of crucible	= 30.02 g
Mass of nickel and crucible	= 31.07 g
Mass of nickel oxide and crucible	= 31.36 g

Determine the following information based on the data given above:

Mass of nickel	=
Mass of nickel oxide	=
Mass of oxygen	=

Based on your calculations, what is the empirical formula for the nickel oxide?

TECHNOLOGY & LEARNING

53. Graphing Calculator Calculate the Molar Mass of a Compound

The graphing calculator can run a program that calculates the molar mass of a compound given the chemical formula for the compound. This program will prompt for the number of elements in the formula, the number of atoms of each element in the formula, and the atomic mass of each element in the formula. It then can be used to find the molar masses of various compounds.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

Note: All answers are written with 2 significant digits beyond the decimal point.

a. What is the molar mass of $BaTiO_3$?
b. What is the molar mass of $PbCl_2$?
c. What is the molar mass of NH_4NO_3?

HANDBOOK SEARCH

54. Review the common reactions of Group 1 metals in the *Elements Handbook* and answer the following:
a. Some of the Group 1 metals react with oxygen to form superoxides. Write the formulas for these compounds.
b. What is the charge on each cation for the formulas you wrote in (a)?
c. How does the charge on the anion vary for oxides, peroxides, and superoxides?

55. Review the common reactions of Group 2 metals in the *Elements Handbook* and answer the following:
a. Some of the Group 2 metals react with oxygen to form oxides. Write the formulas for these compounds.
b. Some of the Group 2 metals react with oxygen to form peroxides. Write the formulas for these compounds.
c. Some of the Group 2 metals react with nitrogen to form nitrides. Write the formulas for these compounds.

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d. Most Group 2 elements form hydrides. What is hydrogen's oxidation state in these compounds?

56. Review the analytical tests for transition metals in the *Elements Handbook* and answer the following:
a. Determine the oxidation state of each metal in the precipitates shown for cadmium, zinc, and lead.
b. Determine the oxidation state of each metal in the complex ions shown for iron, manganese, and cobalt.
c. The copper compound shown is called a coordination compound. The ammonia shown in the formula exists as molecules with no charge. Determine copper's oxidation state in this compound.

57. Review the common reactions of Group 15 elements in the *Elements Handbook* and answer the following:
a. Write formulas for each of the oxides listed for the Group 15 elements.
b. Determine nitrogen's oxidation state in the oxides listed in (a).

RESEARCH & WRITING

58. Nomenclature Biologists who name newly discovered organisms use a system that is structured very much like the one used by chemists in naming compounds. The system used by biologists is called the Linnaeus system, after its creator, Carolus Linnaeus. Research this system in a biology textbook, and then note similarities and differences between the Linnaeus system and chemical nomenclature.

59. Common Chemicals Find out the systematic chemical name and write the chemical formula for each of the following common compounds:
a. baking soda
b. milk of magnesia
c. Epsom salts
d. limestone
e. lye
f. wood alcohol

ALTERNATIVE ASSESSMENT

60. Performance Assessment Your teacher will supply you with a note card with one of the following formulas on it: $NaCH_3COO \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $LiC_2H_3O_2 \cdot 2H_2O$, or $MgSO_4 \cdot 7H_2O$. Design an experiment to determine the percentage of water by mass in the hydrated salt assigned to you. Be sure to explain what steps you will take to ensure that the salt is completely dry. If your teacher approves your design, obtain the salt and perform the experiment. What percentage of water does the salt contain?

61. Both ammonia, NH_3, and ammonium nitrate, NH_4NO_3, are used in fertilizers as a source of nitrogen. Which compound has the higher percentage of nitrogen? Research the physical properties of both compounds, and find out how each is manufactured and used. Explain why each compound has its own particular application. (Consider factors such as the cost of raw ingredients, the ease of manufacture, shipping costs, and so forth.)

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CHAPTER 8

Chemical Equations and Reactions

The evolution of light and heat is an indication that a chemical reaction is taking place.

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Describing Chemical Reactions

SECTION 8-1

Objectives

- List three observations that suggest that a chemical reaction has taken place.
- List three requirements for a correctly written chemical equation.
- Write a word equation and a formula equation for a given chemical reaction.
- Balance a formula equation by inspection.

A *chemical reaction* is the process by which one or more substances are changed into one or more different substances. In any chemical reaction, the original substances are known as the *reactants* and the resulting substances are known as the *products*. According to the law of conservation of mass, the total mass of reactants must equal the total mass of products for any given chemical reaction.

Chemical reactions are described by chemical equations. *A* **chemical equation** *represents, with symbols and formulas, the identities and relative amounts of the reactants and products in a chemical reaction.* For example, the following chemical equation shows that the reactant ammonium dichromate yields the products nitrogen, chromium(III) oxide, and water.

$$(NH_4)_2Cr_2O_7(s) \longrightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$$

This strongly exothermic reaction is shown in Figure 8-1.

Indications of a Chemical Reaction

To know for certain that a chemical reaction has taken place requires evidence that one or more substances have undergone a change in identity. Absolute proof of such a change can be provided only by chemical analysis of the products. However, certain easily observed changes usually indicate that a chemical reaction has occurred.

1. *Evolution of heat and light.* A change in matter that releases energy as both heat and light is strong evidence that a chemical reaction has taken place. For example, you can see in Figure 8-1 that the decomposition of ammonium dichromate is accompanied by the evolution of much heat and light. And you can see evidence that a chemical reaction occurs between natural gas and oxygen if you burn gas for cooking in your house. Some reactions release only heat or only light. But the evolution of heat or light by itself is not necessarily a sign of chemical change because many physical changes also release either heat or light.

FIGURE 8-1 The decomposition of ammonium dichromate proceeds rapidly, releasing energy in the form of light and heat.

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(a) (b)

FIGURE 8-2 (a) The reaction of vinegar and baking soda is evidenced by the production of bubbles of carbon dioxide gas. (b) When water solutions of ammonium sulfide and cadmium nitrate are combined, the yellow precipitate cadmium sulfide forms.

2. *Production of a gas.* The evolution of gas bubbles when two substances are mixed is often evidence of a chemical reaction. For example, bubbles of carbon dioxide gas form immediately when baking soda is mixed with vinegar, in the vigorous reaction that is shown in Figure 8-2(a).
3. *Formation of a precipitate.* Many chemical reactions take place between substances that are dissolved in liquids. If a solid appears after two solutions are mixed, a reaction has likely occurred. *A solid that is produced as a result of a chemical reaction in solution and that separates from the solution is known as a* **precipitate.** A precipitate-forming reaction is shown in Figure 8-2(b).
4. *Color change.* A change in color is often an indication of a chemical reaction.

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Characteristics of Chemical Equations

A properly written chemical equation can summarize any chemical change. The following requirements will aid you in writing and reading chemical equations correctly.

1. *The equation must represent known facts.* All reactants and products must be identified, either through chemical analysis in the laboratory or from sources that give the results of experiments.
2. *The equation must contain the correct formulas for the reactants and products.* Remember what you learned in Chapter 7 about symbols and formulas. Knowledge of the common oxidation states of the elements and of methods of writing formulas will enable you to supply formulas for reactants and products if they are not available. Recall that the elements listed in Table 8-1 exist primarily as diatomic molecules, such as H_2 and O_2. Each of these elements is represented in an equation by its molecular formula. Other elements in the elemental state are usually represented simply by their atomic symbols. For example, iron is represented as Fe and carbon is represented as C. The symbols are not given any subscripts because the elements do not

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TABLE 8-1 *Elements That Normally Exist as Diatomic Molecules*

Element	Symbol	Molecular formula	Physical state at room temperature
Hydrogen	H	H_2	gas
Nitrogen	N	N_2	gas
Oxygen	O	O_2	gas
Fluorine	F	F_2	gas
Chlorine	Cl	Cl_2	gas
Bromine	Br	Br_2	liquid
Iodine	I	I_2	solid

form definite molecular structures. Two exceptions to this rule are sulfur, which is usually written S_8, and phosphorus, which is usually written P_4. In these cases, the formulas reflect each element's unique atomic arrangement in its natural state.

3. *The law of conservation of mass must be satisfied.* Atoms are neither created nor destroyed in ordinary chemical reactions. Therefore, the same number of atoms of each element must appear on each side of a correct chemical equation. To equalize numbers of atoms, coefficients are added where necessary. *A* **coefficient** *is a small whole number that appears in front of a formula in a chemical equation.* Placing a coefficient in front of a formula specifies the relative number of moles of the substance; if no coefficient is written, the coefficient is assumed to be 1. For example, the coefficient 4 in the equation on page 241 indicates that 4 mol of water are produced for each mole of nitrogen and chromium(III) oxide that is produced.

Word and Formula Equations

The first step in writing a chemical equation is to identify the facts to be represented. It is often helpful to write a **word equation,** *an equation in which the reactants and products in a chemical reaction are represented by words.* A word equation has only qualitative (descriptive) meaning. It does not give the whole story because it does not give the quantities of reactants used or products formed.

Consider the reaction of methane, the principal component of natural gas, with oxygen. When methane burns in air, it combines with oxygen to produce carbon dioxide and water vapor. In the reaction, methane and oxygen are the reactants, and carbon dioxide and water are the products. The word equation for the reaction of methane and oxygen is written as follows.

$$\text{methane} + \text{oxygen} \longrightarrow \text{carbon dioxide} + \text{water}$$

The arrow, $\longrightarrow$, is read as *react to yield* or *yield* (also *produce* or *form*). So the equation above is read, "methane and oxygen react to yield

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carbon dioxide and water," or simply, "methane and oxygen yield carbon dioxide and water."

The next step in writing a correct chemical equation is to replace the names of the reactants and products with appropriate symbols and formulas. Methane is a molecular compound composed of one carbon atom and four hydrogen atoms. Its chemical formula is CH_4. Recall that oxygen exists in nature as diatomic molecules; it is therefore represented as O_2. The correct formulas for carbon dioxide and water are CO_2 and H_2O, respectively.

A **formula equation** *represents the reactants and products of a chemical reaction by their symbols or formulas.* The formula equation for the reaction of methane and oxygen is written as follows.

$$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g) \quad \text{(not balanced)}$$

The *g* in parentheses after each formula indicates that the corresponding substance is in the gaseous state. Like a word equation, a formula equation is a qualitative statement. It gives no information about the amounts of reactants or products.

A formula equation meets two of the three requirements for a correct chemical equation. It represents the facts and shows the correct symbols and formulas for the reactants and products. To complete the process of writing a correct equation, the law of conservation of mass must be taken into account. The relative amounts of reactants and products represented in the equation must be adjusted so that the numbers and types of atoms are the same on both sides of the equation. This process is called *balancing an equation* and is carried out by inserting coefficients. Once it is balanced, a formula equation is a correctly written chemical equation.

Look again at the formula equation for the reaction of methane and oxygen.

$$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g) \quad \text{(not balanced)}$$

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To balance the equation, begin by counting atoms of elements that are combined with atoms of other elements and that appear only once on each side of the equation. In this case, we could begin by counting either carbon or hydrogen atoms. Usually, the elements hydrogen and oxygen are balanced only after balancing all other elements in an equation. (You will read more about the rules of balancing equations later in the chapter.) Thus, we begin by counting carbon atoms.

Inspecting the formula equation reveals that there is one carbon atom on each side of the arrow. Therefore, carbon is already balanced in the equation. Counting hydrogen atoms reveals that there are four hydrogen atoms in the reactants but only two in the products. Two additional hydrogen atoms are needed on the right side of the equation. They can be added by placing the coefficient 2 in front of the chemical formula H_2O.

$$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \quad \text{(partially balanced)}$$

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A coefficient multiplies the number of atoms of each element indicated in a chemical formula. Thus, $2H_2O$ represents *four* H atoms and *two* O atoms. To add two more hydrogen atoms to the right side of the equation, one may be tempted to change the subscript in the formula of water so that H_2O becomes H_4O. However, this would be a mistake because changing the subscripts of a chemical formula changes the *identity* of the compound. H_4O is not a product in the combustion of methane. In fact, there is no such compound. One must use only coefficients to change the relative number of atoms in a chemical equation because coefficients change the numbers of atoms without changing the identities of the reactants or products.

Now consider the number of oxygen atoms. There are four oxygen atoms on the right side of the arrow in the partially balanced equation. Yet there are only two oxygen atoms on the left side of the arrow. One can increase the number of oxygen atoms on the left side to four by placing the coefficient 2 in front of the molecular formula for oxygen. This results in a correct chemical equation, or *balanced formula equation,* for the burning of methane in oxygen.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

This reaction is further illustrated in Figure 8-3.

Additional Symbols Used in Chemical Equations

Table 8-2 on page 246 summarizes the symbols commonly used in chemical equations. Sometimes a gaseous product is indicated by an arrow pointing upward, ↑, instead of (g), as shown in the table. A downward arrow, ↓, is often used to show the formation of a precipitate during a reaction in solution.

The conditions under which a reaction takes place are often indicated by placing information above or below the reaction arrow. The word *heat,*

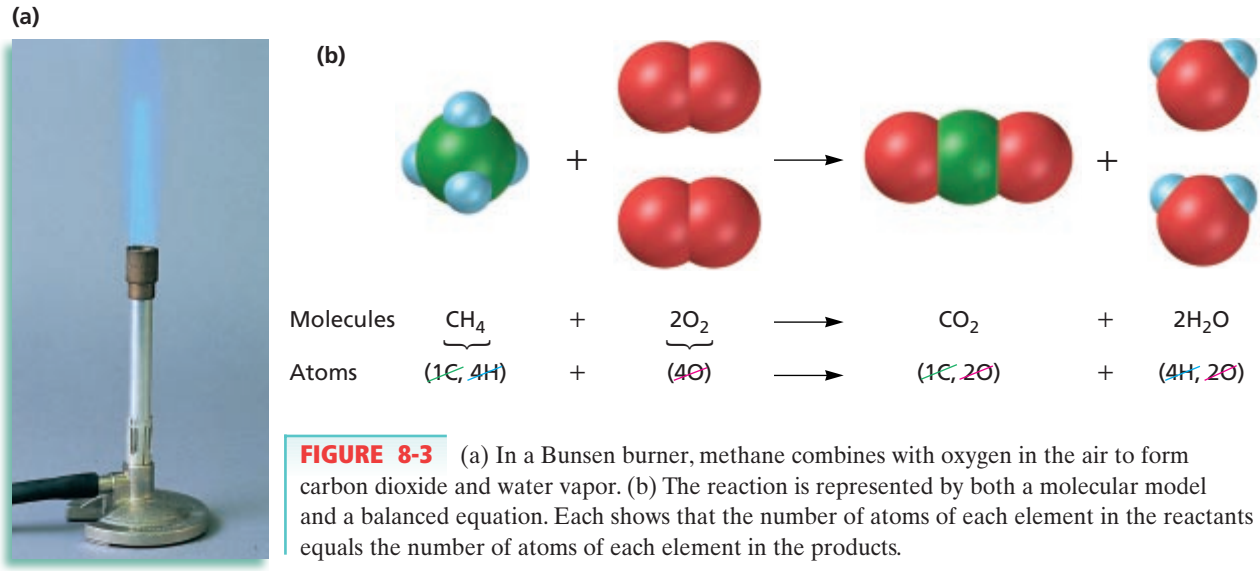

FIGURE 8-3 (a) In a Bunsen burner, methane combines with oxygen in the air to form carbon dioxide and water vapor. (b) The reaction is represented by both a molecular model and a balanced equation. Each shows that the number of atoms of each element in the reactants equals the number of atoms of each element in the products.

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TABLE 8-2 Symbols Used in Chemical Equations

Symbol	Explanation
$\longrightarrow$	"Yields"; indicates result of reaction
$\rightleftharpoons$	Used in place of a single arrow to indicate a reversible reaction
(s)	A reactant or product in the solid state; also used to indicate a precipitate
$\downarrow$	Alternative to (s), but used only to indicate a precipitate
(l)	A reactant or product in the liquid state
(aq)	A reactant or product in an aqueous solution (dissolved in water)
(g)	A reactant or product in the gaseous state
$\uparrow$	Alternative to (g), but used only to indicate a gaseous product
$\xrightarrow{\Delta}$ or $\xrightarrow{\text{heat}}$	Reactants are heated
$\xrightarrow{2\text{ atm}}$	Pressure at which reaction is carried out, in this case 2 atm
$\xrightarrow{\text{pressure}}$	Pressure at which reaction is carried out exceeds normal atmospheric pressure
$\xrightarrow{0^\circ\text{C}}$	Temperature at which reaction is carried out, in this case 0°C
$\xrightarrow{MnO_2}$	Formula of catalyst, in this case manganese dioxide, used to alter the rate of the reaction

symbolized by a Greek capital delta, Δ, indicates that the reactants must be heated. The specific temperature at which a reaction occurs may also be written over the arrow. For some reactions, it is important to specify the pressure at which the reaction occurs or to specify that the pressure must be above normal. Many reactions are speeded up and can take place at lower temperatures in the presence of a *catalyst.* A catalyst is a substance that changes the rate of a chemical reaction but can be recovered unchanged. To show that a catalyst is present, the formula for the catalyst or the word *catalyst* is written over the reaction arrow.

In many reactions, as soon as the products begin to form, they immediately begin to react with each other and re-form the reactants. In other words, the reverse reaction also occurs. The reverse reaction may occur to a greater or lesser degree than the original reaction, depending on the specific reaction and the conditions. *A* **reversible reaction** *is a chemical reaction in which the products re-form the original*

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reactants. The reversibility of a reaction is indicated by writing two arrows pointing in opposite directions. For example, the reversible reaction between iron and water vapor is written as follows.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

With an understanding of all the symbols and formulas used, it is possible to translate a chemical equation into a sentence. Consider the following equation.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

Translated into a sentence, this equation reads, "When heated, solid mercury(II) oxide yields liquid mercury and gaseous oxygen."

It is also possible to write a chemical equation from a sentence describing a reaction. Consider the sentence, "Under pressure and in the presence of a platinum catalyst, gaseous ethene and hydrogen form gaseous ethane." This sentence can be translated into the following equation.

$$C_2H_4(g) + H_2(g) \xrightarrow[Pt]{\text{pressure}} C_2H_6(g)$$

Throughout this chapter we will often include the symbols for physical states (*s, l, g,* and *aq*) in balanced formula equations. You should be able to interpret these symbols when they are used and to supply them when the necessary information is available.

SAMPLE PROBLEM 8-1

Write word and formula equations for the chemical reaction that occurs when solid sodium oxide is added to water at room temperature and forms sodium hydroxide (dissolved in the water). Include symbols for physical states in the formula equation. Then balance the formula equation to give a balanced chemical equation.

SOLUTION

The word equation must show the reactants, sodium oxide and water, to the left of the arrow. The product, sodium hydroxide, must appear to the right of the arrow.

sodium oxide + water ⟶ sodium hydroxide

The word equation is converted to a formula equation by replacing the name of each compound with the appropriate chemical formula. To do this requires knowing that sodium has an oxidation state of +1, that oxygen usually has an oxidation state of –2, and that a hydroxide ion has a charge of 1–.

$$Na_2O + H_2O \longrightarrow NaOH \quad \text{(not balanced)}$$

Adding symbols for the physical states of the reactants and products and the coefficient 2 in front of NaOH produces a balanced chemical equation.

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

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SAMPLE PROBLEM 8-2

Translate the following chemical equation into a sentence:

$$PbCl_2(aq) + Na_2CrO_4(aq) \longrightarrow PbCrO_4(s) + 2NaCl(aq)$$

SOLUTION

Each reactant is an ionic compound and is named according to the rules for such compounds. Both reactants are in aqueous solution. One product is a precipitate and the other remains in solution. The equation is translated as follows: Aqueous solutions of lead(II) chloride and sodium chromate react to produce a precipitate of lead(II) chromate plus sodium chloride in aqueous solution.

PRACTICE

1. Write word and balanced chemical equations for the following reactions. Include symbols for physical states when indicated.
   a. Solid calcium reacts with solid sulfur to produce solid calcium sulfide.
   b. Hydrogen gas reacts with fluorine gas to produce hydrogen fluoride gas. (Hint: See Table 8-1.)
   c. Solid aluminum metal reacts with aqueous zinc chloride to produce solid zinc metal and aqueous aluminum chloride.

2. Translate the following chemical equations into sentences:
   a. $CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$
   b. $NaCl(aq) + AgNO_3(aq) \longrightarrow NaNO_3(aq) + AgCl(s)$

Answer

1. a. calcium + sulfur $\longrightarrow$ calcium sulfide;
   $8Ca(s) + S_8(s) \longrightarrow 8CaS(s)$
   b. hydrogen + fluorine $\longrightarrow$ hydrogen fluoride;
   $H_2(g) + F_2(g) \longrightarrow 2HF(g)$
   c. aluminum + zinc chloride $\longrightarrow$ zinc + aluminum chloride;
   $2Al(s) + 3ZnCl_2(aq) \longrightarrow 3Zn(s) + 2AlCl_3(aq)$

2. a. Liquid carbon disulfide reacts with oxygen gas to produce carbon dioxide gas and sulfur dioxide gas.
   b. Aqueous solutions of sodium chloride and silver nitrate react to produce aqueous sodium nitrate and a precipitate of silver chloride.

Significance of a Chemical Equation

Chemical equations are very useful in doing quantitative chemical work. The arrow in a balanced chemical equation is like an equal sign. And the chemical equation as a whole is similar to an algebraic equation in that it expresses an equality. Let's examine some of the quantitative information revealed by a chemical equation.

1. *The coefficients of a chemical reaction indicate relative, not absolute, amounts of reactants and products.* A chemical equation usually shows the smallest numbers of atoms, molecules, or ions that will satisfy the law of conservation of mass in a given chemical reaction.

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Consider the equation for the formation of hydrogen chloride from hydrogen and chlorine.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

The equation indicates that 1 molecule of hydrogen reacts with 1 molecule of chlorine to produce 2 molecules of hydrogen chloride, giving the following molecular ratio of reactants and products.

$$1 \text{ molecule } H_2 : 1 \text{ molecule } Cl_2 : 2 \text{ molecules HCl}$$

This ratio shows the smallest possible relative amounts of the reaction's reactants and products. To obtain larger relative amounts, we simply multiply each coefficient by the same number. Thus, 20 molecules of hydrogen would react with 20 molecules of chlorine to yield 40 molecules of hydrogen chloride. The reaction can also be considered in terms of amounts in moles: 1 mol of hydrogen molecules reacts with 1 mol of chlorine molecules to yield 2 mol of hydrogen chloride molecules.

2. *The relative masses of the reactants and products of a chemical reaction can be determined from the reaction's coefficients.* Recall from Figure 7-4 on page 224 that an amount of an element or compound in moles can be converted to a mass in grams by multiplying by the appropriate molar mass. We know that 1 mol of hydrogen reacts with 1 mol of chlorine to yield 2 mol of hydrogen chloride. The relative masses of the reactants and products are calculated as follows.

$$1 \text{ mol } H_2 \times \frac{2.02 \text{ g } H_2}{\text{mol } H_2} = 2.02 \text{ g } H_2$$

$$1 \text{ mol } Cl_2 \times \frac{70.90 \text{ g } Cl_2}{\text{mol } Cl_2} = 70.90 \text{ g } Cl_2$$

$$2 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{\text{mol HCl}} = 72.92 \text{ g HCl}$$

The chemical equation shows that 2.02 g of hydrogen will react with 70.90 g of chlorine to yield 72.92 g of hydrogen chloride.

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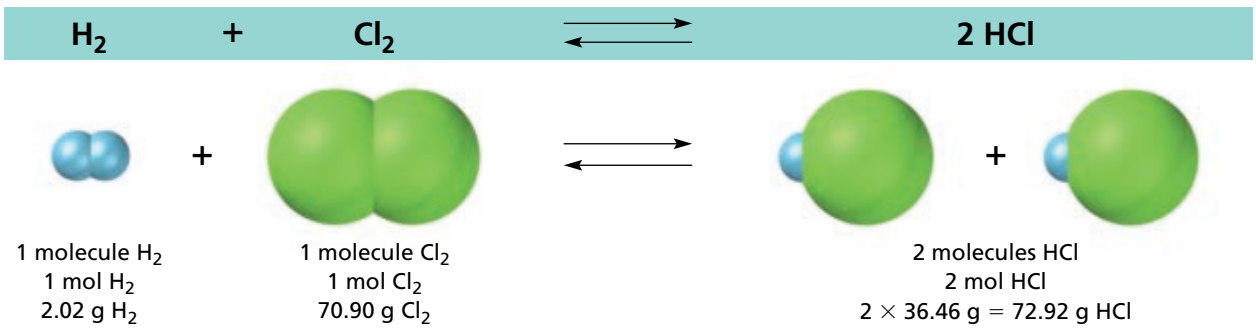
Module 5: Equations and Stoichiometry

FIGURE 8-4 This representation of the reaction of hydrogen and chlorine to yield hydrogen chloride shows several ways to interpret the quantitative information of a chemical reaction.



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3. *The reverse reaction for a chemical equation has the same relative amounts of substances as the forward reaction.* Because a chemical equation is like an algebraic equation, the equality can be read in either direction. Reading the hydrogen chloride formation equation on page 249 from right to left, we can see that 2 molecules of hydrogen chloride break down to form 1 molecule of hydrogen plus 1 molecule of chlorine. Similarly, 2 mol (72.92 g) of hydrogen chloride yield 1 mol (2.02 g) of hydrogen and 1 mol (70.90 g) of chlorine.

We have seen that a chemical equation provides useful quantitative information about a chemical reaction. However, there is also important information that is *not* provided by a chemical equation. For instance, an equation gives no indication of whether a reaction will actually occur. A chemical equation can be written for a reaction that may not even take place. Some guidelines about the types of simple reactions that can be expected to occur are given in Sections 8-2 and 8-3. And later chapters provide additional guidelines for other types of reactions. In all these guidelines, it is important to remember that experimentation forms the basis for confirming that a particular chemical reaction will occur.

In addition, chemical equations give no information about the speed at which reactions occur or about how the bonding between atoms or ions changes during the reaction. These aspects of chemical reactions are discussed in Chapter 17.

FIGURE 8-5 When an electric current is passed through water that has been made slightly conductive, the water molecules break down to yield hydrogen (in tube at right) and oxygen (in tube at left). Bubbles of each gas are evidence of the reaction. Note that twice as much hydrogen as oxygen is produced.

Balancing Chemical Equations

Most of the equations in the remainder of this chapter can be balanced by inspection. The following procedure demonstrates how to master balancing equations by inspection using a step-by-step approach. The equation for the decomposition of water (see Figure 8-5) will be used as an example.

1. *Identify the names of the reactants and the products, and write a word equation.* The word equation for the reaction shown in Figure 8-5 is written as follows.

$$\text{water} \longrightarrow \text{hydrogen} + \text{oxygen}$$

2. *Write a formula equation by substituting correct formulas for the names of the reactants and the products.* We know that the formula for water is H_2O. And recall that both hydrogen and oxygen exist as diatomic molecules. Therefore, their correct formulas are H_2 and O_2, respectively.

$$H_2O(l) \longrightarrow H_2(g) + O_2(g) \quad \text{(not balanced)}$$

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3. *Balance the formula equation according to the law of conservation of mass.* This last step is done by trial and error. Coefficients are changed and the numbers of atoms are counted on both sides of the equation. When the numbers of each type of atom are the same for both the products and the reactants, the equation is balanced. The trial-and-error method of balancing equations is made easier by the use of the following guidelines.

- Balance the different types of atoms one at a time.
- First balance the atoms of elements that are combined and that appear only once on each side of the equation.
- Balance polyatomic ions that appear on both sides of the equation as single units.
- Balance H atoms and O atoms after atoms of all other elements have been balanced.

The formula equation in our example shows that there are two oxygen atoms on the right and only one on the left. To balance oxygen atoms, the number of H_2O molecules must be increased. Placing the coefficient 2 before H_2O gives the necessary two oxygen atoms on the left.

$$2H_2O(l) \longrightarrow H_2(g) + O_2(g) \quad \text{(partially balanced)}$$

The coefficient 2 in front of H_2O has upset the balance of hydrogen atoms. Placing the coefficient 2 in front of hydrogen, H_2, on the right, gives an equal number of hydrogen atoms (4) on both sides of the equation.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

4. *Count atoms to be sure that the equation is balanced.* Make sure that equal numbers of atoms of each element appear on both sides of the arrow.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$
$$(4H + 2O) = (4H) + (2O)$$

Occasionally at this point, the coefficients do not represent the smallest possible whole-number ratio of reactants and products. When this happens, the coefficients should be divided by their greatest common factor in order to obtain the smallest possible whole-number coefficients.

Balancing chemical equations by inspection becomes easier as you gain experience. Learn to avoid the most common mistakes: (1) writing incorrect chemical formulas for reactants or products and (2) trying to balance an equation by changing subscripts. Remember that subscripts cannot be added, deleted, or changed. Eventually, you will probably be able to skip writing the word equation and each separate step. However, *do not* leave out the final step of counting atoms to be sure the equation is balanced.

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SAMPLE PROBLEM 8-3

The reaction of zinc with aqueous hydrochloric acid produces a solution of zinc chloride and hydrogen gas. This reaction is shown at right in Figure 8-6. Write a balanced chemical equation for the reaction.

FIGURE 8-6 Solid zinc reacts with hydrochloric acid to form aqueous zinc chloride and hydrogen gas.

SOLUTION

1 ANALYZE

Write the word equation.

$$\text{zinc} + \text{hydrochloric acid} \longrightarrow \text{zinc chloride} + \text{hydrogen}$$

2 PLAN

Write the formula equation.

$$Zn(s) + HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g) \quad \text{(not balanced)}$$

3 COMPUTE

Adjust the coefficients. Note that chlorine and hydrogen each appear only once on each side of the equation. We balance chlorine first because it is combined on both sides of the equation. Also, recall from the guidelines on page 251 that hydrogen and oxygen are balanced only after all other elements in the reaction are balanced. To balance chlorine, we place the coefficient 2 before HCl. Two molecules of hydrogen chloride also yield the required two hydrogen atoms on the right. Finally, note that there is one zinc atom on each side in the formula equation. Therefore, no further coefficients are needed.

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

4 EVALUATE

Count atoms to check balance.

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$
$$(1Zn) + (2H + 2Cl) = (1Zn + 2Cl) + (2H)$$

The equation is balanced.

PRACTICE

1. Write word, formula, and balanced chemical equations for each of the following reactions:
   a. Magnesium and hydrochloric acid react to produce magnesium chloride and hydrogen.
   b. Aqueous nitric acid reacts with solid magnesium hydroxide to produce aqueous magnesium nitrate and water.

Answer

1. a. Word: magnesium + hydrochloric acid $\longrightarrow$ magnesium chloride + hydrogen

   Formula: $Mg + HCl \longrightarrow MgCl_2 + H_2$

   Balanced: $Mg + 2HCl \longrightarrow MgCl_2 + H_2$

   b. Word: nitric acid + magnesium hydroxide $\longrightarrow$ magnesium nitrate + water

   Formula: $HNO_3(aq) + Mg(OH)_2(s) \longrightarrow Mg(NO_3)_2(aq) + H_2O(l)$

   Balanced: $2HNO_3(aq) + Mg(OH)_2(s) \longrightarrow Mg(NO_3)_2(aq) + 2H_2O(l)$

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SAMPLE PROBLEM 8-4

Solid aluminum carbide, Al_4C_3, reacts with water to produce methane gas and solid aluminum hydroxide. Write a balanced chemical equation for this reaction.

SOLUTION

The reactants are aluminum carbide and water. The products are methane and aluminum hydroxide. The formula equation is written as follows.

$$Al_4C_3(s) + H_2O(l) \longrightarrow CH_4(g) + Al(OH)_3(s) \quad \text{(not balanced)}$$

Begin balancing the formula equation by counting either aluminum atoms or carbon atoms. (Remember that hydrogen and oxygen atoms are balanced last.) There are four Al atoms on the left. To balance Al atoms, place the coefficient 4 before $Al(OH)_3$ on the right.

$$Al_4C_3(s) + H_2O(l) \longrightarrow CH_4(g) + 4Al(OH)_3(s) \quad \text{(partially balanced)}$$

Now balance the carbon atoms. With three C atoms on the left, the coefficient 3 must be placed before CH_4 on the right.

$$Al_4C_3(s) + H_2O(l) \longrightarrow 3CH_4(g) + 4Al(OH)_3(s) \quad \text{(partially balanced)}$$

Balance oxygen atoms next because oxygen, unlike hydrogen, appears only once on each side of the equation. There is one O atom on the left and 12 O atoms in the four $Al(OH)_3$ formula units on the right. Placing the coefficient 12 before H_2O balances the O atoms.

$$Al_4C_3(s) + 12H_2O(l) \longrightarrow 3CH_4(g) + 4Al(OH)_3(s)$$

This leaves the hydrogen atoms to be balanced. There are 24 H atoms on the left. On the right, there are 12 H atoms in the methane molecules and 12 in the aluminum hydroxide formula units, totaling 24 H atoms. The H atoms are balanced.

$$\begin{array}{ccccc} Al_4C_3(s) & + & 12H_2O(l) & \longrightarrow & 3CH_4(g) + 4Al(OH)_3(s) \\ (\cancel{4Al} + \cancel{3C}) & + & (\cancel{24H} + \cancel{12O}) & = & (\cancel{3C} + \cancel{12H}) + (\cancel{4Al} + \cancel{12H} + \cancel{12O}) \end{array}$$

The equation is balanced.

SAMPLE PROBLEM 8-5

Aluminum sulfate and calcium hydroxide are used in a water-purification process. When added to water, they dissolve and react to produce two insoluble products, aluminum hydroxide and calcium sulfate. These products settle out, taking suspended solid impurities with them. Write a balanced chemical equation for the reaction.

SOLUTION

Each of the reactants and products is an ionic compound. Recall from Chapter 7 that the formulas of ionic compounds are determined by the charges of the ions composing each compound. The formula reaction is thus written as follows.

$$Al_2(SO_4)_3 + Ca(OH)_2 \longrightarrow Al(OH)_3 + CaSO_4 \quad \text{(not balanced)}$$

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There is one Ca atom on each side of the equation, so the calcium atoms are already balanced. There are two Al atoms on the left and one Al atom on the right. Placing the coefficient 2 in front of $Al(OH)_3$ produces the same number of Al atoms on each side of the equation.

$$Al_2(SO_4)_3 + Ca(OH)_2 \longrightarrow 2Al(OH)_3 + CaSO_4 \quad \text{(partially balanced)}$$

Next, checking SO_4^{2-} ions shows that there are three SO_4^{2-} ions on the left side of the equation and only one on the right side. Placing the coefficient 3 before $CaSO_4$ gives an equal number of SO_4^{2-} ions on each side.

$$Al_2(SO_4)_3 + Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 \quad \text{(partially balanced)}$$

There are now three Ca atoms on the right, however. By placing the coefficient 3 in front of $Ca(OH)_2$, we once again have an equal number of Ca atoms on each side. This last step also gives six OH^- ions on both sides of the equation.

$$Al_2(SO_4)_3(aq) + 3Ca(OH)_2(aq) \longrightarrow 2Al(OH)_3(s) + 3CaSO_4(s)$$
$$(2Al + 3SO_4^{2-}) + (3Ca + 6OH^-) = (2Al + 6OH^-) + (3Ca + 3SO_4^{2-})$$

The equation is balanced.

PRACTICE

1. Write balanced chemical equations for each of the following reactions:
   a. Solid sodium combines with chlorine gas to produce solid sodium chloride.
   b. When solid copper reacts with aqueous silver nitrate, the products are aqueous copper(II) nitrate and solid silver.
   c. In a blast furnace, the reaction between solid iron(III) oxide and carbon monoxide gas produces solid iron and carbon dioxide gas.

Answer

1. a. $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

   b. $Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$

   c. $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

SECTION REVIEW

1. Describe the differences between word equations, formula equations, and chemical equations.
2. Write word and formula equations for the reaction in which aqueous solutions of sulfuric acid and sodium hydroxide react to form aqueous sodium sulfate and water.
3. Translate the following chemical equations into sentences:
   a. $2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$
   b. $2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$
4. Write the word, formula, and chemical equations for the reaction between hydrogen sulfide gas and oxygen gas that produces sulfur dioxide gas and water vapor.
5. Write the chemical equation for each of the following reactions:
   a. ammonium chloride + calcium hydroxide $\longrightarrow$ calcium chloride + ammonia + water
   b. hexane, C_6H_{14}, + oxygen $\longrightarrow$ carbon dioxide + water

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A Chemical Mystery

From "The Chemical Adventures of Sherlock Holmes: The Hound of Henry Armitage" by Thomas G. Waddell and Thomas R. Rybolt in *The Journal of Chemical Education*

"I knew it," the old man snapped. "He was poisoned, wasn't he? . . ."

. . . But Holmes was not listening. He had picked up the dog's bowl, now empty, and was vigorously sniffing, not unlike the hound itself, at the crusted remains of the last meal . . .

An hour later I was in my chair at 221B Baker Street. Holmes was in his laboratory and I could hear him humming. In the background was the usual clattering and clanking of laboratory equipment . . . Suddenly, Holmes called to me.

"Watson, come here. I need you." . . . He calmly scribbled an equation on a slip of paper and handed it to me. "If you can balance this equation, Watson, you can solve this mystery." I looked at the page as best I could and saw the following equation with the formula of a reactant clearly missing.

$$C_6H_5NH_2 + 3KOH + \_\_\_\_ \Rightarrow C_6H_5NC + 3KCl + 3H_2O$$

Holmes paced back and forth with his hands clasped behind his back. "One part aniline, three parts potassium hydroxide, and one part unknown poison yields one part phenylisocyanide, three parts potassium chloride, and three parts water. The missing reactant can be identified by balancing the equation with respect to all the atoms involved. The product phenylisocyanide . . . is derived by this reaction from that missing chemical which was the poison deliberately placed in the hound's food."

"I can follow you part of the way," I submitted. "You undoubtedly detected a foreign substance in the dog food due to a characteristic aroma."

"Correct, Watson," Holmes replied. "And as a chemist I knew immediately that the poison was *volatile* . . . We observed the compound to be a liquid at room temperature, immiscible with water, and having a density greater than 1.00 g/mL! The unpleasant sweetness of it was also very helpful. The possibilities were quite limited at that point, Watson . . .

I formed a working hypothesis and performed a known chemical test for such a poisonous liquid meeting all these criteria. Did you balance the equation, Watson? The equation confirms it!"

"I can do it, Holmes. I remember that much chemistry. Let me see . . . the missing reactant must have chlorine . . . 3 units to balance Cl in the product!"

"Very good, Watson. Go on with it."

"It gets more complex, now, but look, there is one extra carbon atom in the products! Is CCl_3 the compound?"

"Carbon makes *four* bonds, Watson, not three," said Holmes with a frown.

"I have it! $CHCl_3$ balances the equation! That's *chloroform*, Holmes! Of course. It all is consistent."

Reading for Meaning

Can you infer the meaning of the word *volatile* from the story? Write down your definition. Then compare your definition with one from a chemical or technical dictionary.

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SCILINKS NSTA

TOPIC: Chloroform
GO TO: www.scilinks.org
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SECTION 8-2

OBJECTIVES

- Define and give general equations for *synthesis, decomposition, single-replacement,* and *double-replacement* reactions.
- Classify a reaction as synthesis, decomposition, single-replacement, double-replacement, or combustion.
- List three types of synthesis reactions and six types of decomposition reactions.
- List four types of single-replacement reactions and three types of double-replacement reactions.
- Predict the products of simple reactions given the reactants.

Types of Chemical Reactions

Thousands of known chemical reactions occur in living systems, in industrial processes, and in chemical laboratories. Often it is necessary to predict the products formed in one of these reactions. Memorizing the equations for so many chemical reactions would be a difficult task. It is therefore more useful and realistic to classify reactions according to various similarities and regularities. This general information about reaction types can then be used to predict the products of specific reactions.

There are several different ways to classify chemical reactions, and none are entirely satisfactory. The classification scheme described in this section provides an introduction to five basic types of reactions: synthesis, decomposition, single-replacement, double-replacement, and combustion. In later chapters you will be introduced to categories that are useful in classifying other types of chemical reactions.

Synthesis Reactions

In a **synthesis reaction,** *also known as a* **composition reaction,** *two or more substances combine to form a new compound.* This type of reaction is represented by the following general equation.

$$A + X \longrightarrow AX$$

A and X can be elements or compounds. AX is a compound. The following examples illustrate several kinds of synthesis reactions.

Reactions of Elements with Oxygen and Sulfur

One simple type of synthesis reaction is the combination of an element with oxygen to produce an *oxide* of the element. Almost all metals react with oxygen to form oxides. For example, when a thin strip of magnesium metal is placed in an open flame, it burns with bright white light. When the metal strip is completely burned, only a fine white powder of magnesium oxide is left. This chemical reaction, shown in Figure 8-7, is represented by the following equation.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

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The other Group 2 elements react in a similar manner, forming oxides with the formula MO, where M represents the metal. The Group 1 metals form oxides with the formula M_2O, for example, Li_2O. The Group 1 and Group 2 elements react similarly with sulfur, forming *sulfides* with the formulas M_2S and MS, respectively. Examples of these types of synthesis reactions are shown below.

$$16Rb(s) + S_8(s) \longrightarrow 8Rb_2S(s)$$
$$8Ba(s) + S_8(s) \longrightarrow 8BaS(s)$$

Some metals, such as iron, combine with oxygen to produce two different oxides.

$$2Fe(s) + O_2(g) \longrightarrow 2FeO(s)$$
$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

In the product of the first reaction, iron is in an oxidation state of +2. In the product of the second reaction, iron is in an oxidation state of +3. The particular oxide formed depends on the conditions surrounding the reactants. Both oxides are shown below in Figure 8-8.

Nonmetals also undergo synthesis reactions with oxygen to form oxides. Sulfur, for example, reacts with oxygen to form sulfur dioxide. And when carbon is burned in air, carbon dioxide is produced.

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$
$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

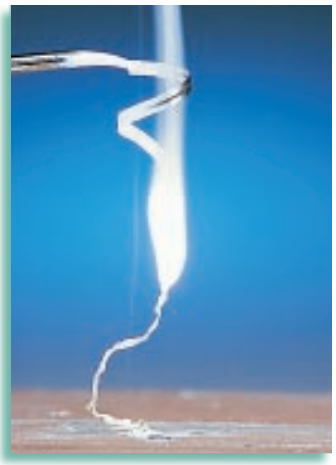
In a limited supply of oxygen, carbon monoxide is formed.

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

Hydrogen reacts with oxygen to form dihydrogen monoxide, better known as water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

(a)



(b)

FIGURE 8-7 Magnesium, Mg, pictured in (a), undergoes a synthesis reaction with oxygen, O_2, in the air to produce magnesium oxide, MgO, as shown in (b).

(a)

(b)

FIGURE 8-8 Iron, Fe, and oxygen, O_2, combine to form two different oxides: (a) iron(II) oxide, FeO, and (b) iron(III) oxide, Fe_2O_3.

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Reactions of Metals with Halogens

Most metals react with the Group 17 elements, the halogens, to form either ionic or covalent compounds. For example, Group 1 metals react with halogens to form ionic compounds with the formula MX, where M is the metal and X is the halogen. Examples of this type of synthesis reaction include the reactions of sodium with chlorine and potassium with iodine.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$
$$2K(s) + I_2(g) \longrightarrow 2KI(s)$$

Group 2 metals react with the halogens to form ionic compounds with the formula MX_2.

$$Mg(s) + F_2(g) \longrightarrow MgF_2(s)$$
$$Sr(s) + Br_2(l) \longrightarrow SrBr_2(s)$$

The halogens undergo synthesis reactions with many different metals. Fluorine in particular is so reactive that it combines with almost all metals. For example, fluorine reacts with sodium to produce sodium fluoride. Similarly, it reacts with cobalt to form cobalt(III) fluoride and with uranium to form uranium(VI) fluoride.

$$2Na(s) + F_2(g) \longrightarrow 2NaF(s)$$
$$2Co(s) + 3F_2(g) \longrightarrow 2CoF_3(s)$$
$$U(s) + 3F_2(g) \longrightarrow UF_6(g)$$

Sodium fluoride, NaF, is added to municipal water supplies in trace amounts to provide fluoride ions, which help to prevent tooth decay in the people who drink the water. Cobalt(III) fluoride, CoF_3, is a strong fluorinating agent. And natural uranium is converted to uranium(VI) fluoride, UF_6, as the first step in the production of uranium for use in nuclear power plants.

ANTACID TABLETS
ACTIVE INGREDIENTS: Each tablet contains a balanced
Aluminum hydroxide
Calcium Hydroxide and 20 mg
INACTIVE INGREDIENTS: Colloidal Silicon Dioxide,
Magnesium Stearate, Mannitol, Sodium Saccharin

FIGURE 8-9 Calcium hydroxide, a base, can be used to *neutralize* hydrochloric acid in your stomach. You will read more about acids, bases, and neutralization in Chapter 15.

Synthesis Reactions with Oxides

Active metals are highly reactive metals. Oxides of active metals react with water to produce metal hydroxides. For example, calcium oxide reacts with water to form calcium hydroxide, an ingredient in some stomach antacids.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

Calcium oxide, CaO, also known as lime or quicklime, is manufactured in large quantities. The addition of water to lime to produce $Ca(OH)_2$, which is also known as slaked lime, is a crucial step in the setting of cement.

Many oxides of nonmetals in the upper right portion of the periodic table react with water to produce oxyacids. For example, sulfur dioxide, SO_2, reacts with water to produce sulfurous acid.

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$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$

In air polluted with SO_2, sulfurous acid further reacts with oxygen to form sulfuric acid, one of the main ingredients in *acid rain*.

$$2H_2SO_3(aq) + O_2(g) \longrightarrow 2H_2SO_4(aq)$$

Certain metal oxides and nonmetal oxides react with each other in synthesis reactions to form salts. For example, calcium sulfite is formed by the reaction of calcium oxide and sulfur dioxide.

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

Decomposition Reactions

In a **decomposition reaction,** *a single compound undergoes a reaction that produces two or more simpler substances.* Decomposition reactions are the opposite of synthesis reactions and are represented by the following general equation.

$$AX \longrightarrow A + X$$

AX is a compound. A and X can be elements or compounds.

Most decomposition reactions take place only when energy in the form of electricity or heat is added. Examples of several types of decomposition reactions are given in the following sections.

Decomposition of Binary Compounds

The simplest kind of decomposition reaction is the decomposition of a binary compound into its elements. We have already examined one example of a decomposition reaction. Figure 8-5 on page 250 shows that passing an electric current through water will decompose the water into its constituent elements, hydrogen and oxygen.

$$2H_2O(l) \xrightarrow{\text{electricity}} 2H_2(g) + O_2(g)$$

The decomposition of a substance by an electric current is called **electrolysis.**

Oxides of the less-active metals, which are located in the lower center of the periodic table, decompose into their elements when heated. Joseph Priestley discovered oxygen through such a decomposition reaction in 1774, when he heated mercury(II) oxide to produce mercury and oxygen.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

This reaction is shown in Figure 8-10 on page 260.

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FIGURE 8-10 When mercury(II) oxide (the red-orange substance in the bottom of the test tube) is heated, it decomposes into oxygen and metallic mercury, which can be seen as droplets on the inside wall of the test tube.

Decomposition of Metal Carbonates

When a metal carbonate is heated, it breaks down to produce a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes to produce calcium oxide and carbon dioxide.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

Decomposition of Metal Hydroxides

All metal hydroxides except those containing Group 1 metals decompose when heated to yield metal oxides and water. For example, calcium hydroxide decomposes to produce calcium oxide and water.

$$Ca(OH)_2(s) \xrightarrow{\Delta} CaO(s) + H_2O(g)$$

Decomposition of Metal Chlorates

When a metal chlorate is heated, it decomposes to produce a metal chloride and oxygen. For example, potassium chlorate, $KClO_3$, decomposes in the presence of the catalyst $MnO_2(s)$ to produce potassium chloride and oxygen.

$$2KClO_3(s) \xrightarrow[MnO_2(s)]{\Delta} 2KCl(s) + 3O_2(g)$$

Decomposition of Acids

Certain acids decompose into nonmetal oxides and water. Carbonic acid is unstable and decomposes readily at room temperature to produce carbon dioxide and water.

$$H_2CO_3(aq) \longrightarrow CO_2(g) + H_2O(l)$$

When heated, sulfuric acid decomposes into sulfur trioxide and water.

$$H_2SO_4(aq) \xrightarrow{\Delta} SO_3(g) + H_2O(l)$$

Sulfurous acid, H_2SO_3, decomposes similarly.

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Single-Replacement Reactions

In a **single-replacement reaction,** *also known as a* **displacement reaction,** *one element replaces a similar element in a compound.* Many single-replacement reactions take place in aqueous solution. The amount of energy involved in this type of reaction is usually smaller than the amount involved in synthesis or decomposition reactions. Single-replacement reactions can be represented by the following general equations.

$$A + BX \longrightarrow AX + B$$
or
$$Y + BX \longrightarrow BY + X$$

A, B, X, and Y are elements. AX, BX, and BY are compounds.

Replacement of a Metal in a Compound by Another Metal

Aluminum is more active than lead. When solid aluminum is placed in aqueous lead(II) nitrate, $Pb(NO_3)_2(aq)$, the aluminum replaces the lead. Solid lead and aqueous aluminum nitrate are formed.

$$2Al(s) + 3Pb(NO_3)_2(aq) \longrightarrow 3Pb(s) + 2Al(NO_3)_3(aq)$$

Replacement of Hydrogen in Water by a Metal

The most-active metals, such as those in Group 1, react vigorously with water to produce metal hydroxides and hydrogen. For example, sodium reacts with water to form sodium hydroxide and hydrogen gas.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

Less-active metals, such as iron, react with steam to form a metal oxide and hydrogen gas.

$$3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$

Replacement of Hydrogen in an Acid by a Metal

The more-active metals react with certain acidic solutions, such as hydrochloric acid and dilute sulfuric acid, replacing the hydrogen in the acid. The reaction products are a metal compound (a salt) and hydrogen gas. For example, when solid magnesium reacts with hydrochloric acid, as shown in Figure 8-11, the reaction products are hydrogen gas and aqueous magnesium chloride.

$$Mg(s) + 2HCl(aq) \longrightarrow H_2(g) + MgCl_2(aq)$$

Replacement of Halogens

In another type of single-replacement reaction, one halogen replaces another halogen in a compound. Fluorine is the most-active halogen. As

FIGURE 8-11 In this single-replacement reaction, the hydrogen in hydrochloric acid, HCl, is replaced by magnesium, Mg.

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such, it can replace any of the other halogens in their compounds. Each halogen is less active than the one above it in the periodic table. Therefore, in Group 17 each element can replace any element below it, but not any element above it. For example, while chlorine can replace bromine in potassium bromide, it cannot replace fluorine in potassium fluoride. The reaction of chlorine with potassium bromide produces bromine and potassium chloride, whereas the combination of fluorine and sodium chloride produces sodium fluoride and solid chlorine.

$$Cl_2(g) + 2KBr(aq) \longrightarrow 2KCl(aq) + Br_2(l)$$
$$F_2(g) + 2NaCl(aq) \longrightarrow 2NaF(aq) + Cl_2(g)$$
$$Br_2(l) + KCl(aq) \longrightarrow \text{no reaction}$$

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Double-Replacement Reactions

In **double-replacement reactions,** *the ions of two compounds exchange places in an aqueous solution to form two new compounds.* One of the compounds formed is usually a precipitate, an insoluble gas that bubbles out of the solution, or a molecular compound, usually water. The other compound is often soluble and remains dissolved in solution. A double-replacement reaction is represented by the following general equation.

$$AX + BY \longrightarrow AY + BX$$

A, X, B, and Y in the reactants represent ions. AY and BX represent ionic or molecular compounds.

Formation of a Precipitate

The formation of a precipitate occurs when the cations of one reactant combine with the anions of another reactant to form an insoluble or slightly soluble compound. For example, when an aqueous solution of potassium iodide is added to an aqueous solution of lead(II) nitrate, the yellow precipitate lead(II) iodide forms. This is shown in Figure 8-12.

$$2KI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$

The precipitate forms as a result of the very strong attractive forces between the Pb^{2+} cations and the I^- anions. The other product is the water-soluble salt potassium nitrate, KNO_3. The potassium and nitrate ions do not take part in the reaction. They remain in solution as aqueous ions. The guidelines that help identify which ions form a precipitate and which ions remain in solution are developed in Chapter 14.

FIGURE 8-12 The double-replacement reaction between aqueous lead(II) nitrate, $Pb(NO_3)_2(aq)$, and aqueous potassium iodide, $KI(aq)$, yields the precipitate lead(II) iodide, $PbI_2(s)$.

Formation of a Gas

In some double-replacement reactions, one of the products is an insoluble gas that bubbles out of the mixture. For example, iron(II) sulfide

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reacts with hydrochloric acid to form hydrogen sulfide gas and iron(II) chloride.

$$FeS(s) + 2HCl(aq) \longrightarrow H_2S(g) + FeCl_2(aq)$$

Formation of Water

In some double-replacement reactions, a very stable molecular compound, such as water, is one of the products. For example, hydrochloric acid reacts with an aqueous solution of sodium hydroxide to yield aqueous sodium chloride and water.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

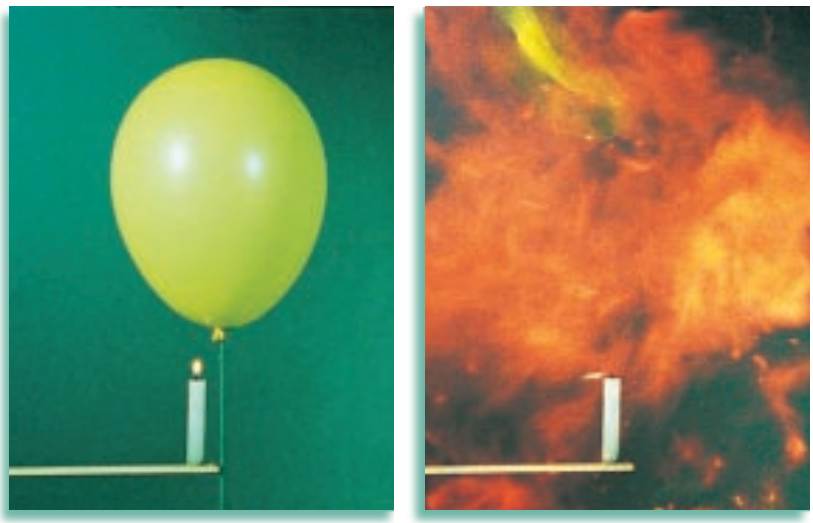
Combustion Reactions

In a **combustion reaction,** *a substance combines with oxygen, releasing a large amount of energy in the form of light and heat.* The combustion of hydrogen is shown below in Figure 8-13. The reaction's product is water vapor.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The burning of natural gas, propane, gasoline, and wood are also examples of combustion reactions. For example, the burning of propane, C_3H_8, results in the production of carbon dioxide and water vapor.

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$



(a) (b)

FIGURE 8-13 (a) The candle supplies heat to the hydrogen and oxygen in the balloon, triggering the explosive combustion reaction shown in (b).

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Quick LAB

Balancing Equations Using Models

Wear Safety Goggles and an Apron.

Materials

- large and small gumdrops in at least four different colors
- toothpicks

Question

How can molecular models and formula-unit ionic models be used to balance chemical equations and classify chemical reactions?

Procedure

Examine the partial equations in Groups A–E. Using different-colored gumdrops to represent atoms of different elements, make models of the reactions by connecting the appropriate "atoms" with toothpicks. Use your models to (1) balance equations (a) and (b) in each group, (2) determine the products for reaction (c) in each group, and (3) complete and balance each equation (c). Finally, (4) classify each group of reactions by type.

Group A
a. $H_2 + Cl_2 \longrightarrow HCl$
b. $Mg + O_2 \longrightarrow MgO$
c. $BaO + H_2O \longrightarrow$ _____

Group B
a. $H_2CO_3 \longrightarrow CO_2 + H_2O$
b. $KClO_3 \longrightarrow KCl + O_2$
c. $H_2O \xrightarrow{\text{electricity}}$ _____

Group C
a. $Ca + H_2O \longrightarrow Ca(OH)_2 + H_2$
b. $KI + Br_2 \longrightarrow KBr + I_2$
c. $Zn + HCl \longrightarrow$ _____

Group D
a. $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$
b. $FeS + HCl \longrightarrow FeCl_2 + H_2S$
c. $H_2SO_4 + KOH \longrightarrow$ _____

Group E
a. $CH_4 + O_2 \longrightarrow CO_2 + H_2O$
b. $CO + O_2 \longrightarrow CO_2$
c. $C_3H_8 + O_2 \longrightarrow$ _____

SECTION REVIEW

1. List five types of chemical reactions.
2. Classify each of the following reactions as synthesis, decomposition, single-replacement, double-replacement, or combustion:
   a. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
   b. $2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$
   c. $2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$
   d. $2C_6H_{14}(l) + 19O_2(g) \longrightarrow 12CO_2(g) + 14H_2O(l)$
   e. $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$
   f. $BaO(s) + H_2O(l) \longrightarrow Ba(OH)_2(aq)$
   g. $AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$
3. For each of the following reactions, identify the missing reactant(s) or products(s) and then balance the resulting equation. Note that each empty slot may require one or more substances.
   a. synthesis: _____ $\longrightarrow Li_2O$
   b. decomposition: $Mg(ClO_3)_2 \longrightarrow$ _____
   c. single-replacement: $Na + H_2O \longrightarrow$ _____
   d. double-replacement: $HNO_3 + Ca(OH)_2 \longrightarrow$ _____
   e. combustion: $C_5H_{12} + O_2 \longrightarrow$ _____
4. For each of the following reactions, write the missing product(s) and then balance the resulting equation. Identify each reaction by type.
   a. $Br_2 + KI \longrightarrow$ _____
   b. $Zn + HCl \longrightarrow$ _____
   c. $Ca + Cl_2 \longrightarrow$ _____
   d. $NaClO_3 \xrightarrow{\Delta}$ _____
   e. $C_7H_{14} + O_2 \longrightarrow$ _____
   f. $CuCl_2 + Na_2S \longrightarrow$ _____

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Activity Series of the Elements

SECTION 8-3

OBJECTIVES

- Explain the significance of an activity series.
- Use an activity series to predict whether a given reaction will occur and what the products will be.

The ability of an element to react is referred to as the element's *activity*. The more readily an element reacts with other substances, the greater its activity is. *An* **activity series** *is a list of elements organized according to the ease with which the elements undergo certain chemical reactions*. For metals, greater activity means a greater ease of *loss* of electrons, to form positive ions. For nonmetals, greater activity means a greater ease of *gain* of electrons, to form negative ions.

The order in which the elements are listed is usually determined by single-replacement reactions. The most-active element, placed at the top in the series, can replace each of the elements below it from a compound in a single-replacement reaction. An element farther down can replace any element below it but not any above it. For example, in the discussion of single-replacement reactions in Section 8-2, it was noted that each halogen will react to replace any halogen listed below it in the periodic table. Therefore, an activity series for the Group 17 elements lists them in the same order, from top to bottom, as they appear in the periodic table. This is shown in Table 8-3 on page 266.

As mentioned in Section 8-1, the fact that a chemical equation can be written does not necessarily mean that the reaction it represents will actually take place. Activity series are used to help predict whether certain chemical reactions will occur. For example, according to the activity series for metals in Table 8-3, aluminum replaces zinc. Therefore, we could predict that the following reaction does occur.

$$2Al(s) + 3ZnCl_2(aq) \longrightarrow 3Zn(s) + 2AlCl_3(aq)$$

Cobalt, however, cannot replace sodium. Therefore, we write the following.

$$Co(s) + 2NaCl(aq) \longrightarrow \text{no reaction}$$

It is important to remember that like many other aids used to predict the products of chemical reactions, activity series are based on experiment. The information that they contain is used as a general guide for predicting reaction outcomes. For example, the activity series reflects the fact that some metals (potassium, for example) react vigorously with water and acids, replacing hydrogen to form new compounds. Other metals, such as iron or zinc, replace hydrogen in acids such as hydrochloric acid but react with water only when the water is hot

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enough to become steam. Nickel, on the other hand, will replace hydrogen in acids but will not react with steam at all. And gold will not react with acid or water, either as a liquid or as steam. Such experimental observations are the basis for the activity series shown in Table 8-3.

TABLE 8-3 *Activity Series of the Elements*

Activity of metals		Activity of halogen nonmetals
Li Rb K Ba Sr Ca Na	React with cold H_2O and acids, replacing hydrogen. React with oxygen, forming oxides.	F_2 Cl_2 Br_2 I_2
Mg Al Mn Zn Cr Fe Cd	React with steam (but not cold water) and acids, replacing hydrogen. React with oxygen, forming oxides.	
Co Ni Sn Pb	Do not react with water. React with acids, replacing hydrogen. React with oxygen, forming oxides.	
H_2 Sb Bi Cu Hg	React with oxygen, forming oxides.	
Ag Pt Au	Fairly unreactive, forming oxides only indirectly.	

SAMPLE PROBLEM 8-6

Using the activity series shown in Table 8-3, explain whether each of the possible reactions listed below will occur. For those reactions that will occur, predict what the products will be.

a. $Zn(s) + H_2O(l) \xrightarrow{50°C}$ _____
b. $Sn(s) + O_2(g) \longrightarrow$ _____
c. $Cd(s) + Pb(NO_3)_2(aq) \longrightarrow$ _____
d. $Cu(s) + HCl(aq) \longrightarrow$ _____

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SOLUTION

a. This is a reaction between a metal and water at 50°C. Zinc reacts with water only when it is hot enough to be steam. Therefore, no reaction will occur.

b. Any metal more active than silver will react with oxygen to form an oxide. Tin is above silver in the activity series. Therefore, a reaction will occur, and the product will be a tin oxide, either SnO or SnO_2.

c. An element will replace any element below it in the activity series from a compound in aqueous solution. Cadmium is above lead, and therefore a reaction will occur to produce lead, Pb, and cadmium nitrate, $Cd(NO_3)_2$.

d. Any metal more active than hydrogen will replace hydrogen from an acid. Copper is not above hydrogen in the series. Therefore, no reaction will occur.

PRACTICE

1. Using the activity series shown in Table 8-3, predict whether each of the possible reactions listed below will occur. For the reactions that will occur, write the products and balance the equation.

a. $Cr(s) + H_2O(l) \longrightarrow$ _____

b. $Pt(s) + O_2(g) \longrightarrow$ _____

c. $Cd(s) + 2HBr(aq) \longrightarrow$ _____

d. $Mg(s) + \text{steam} \longrightarrow$ _____

2. Identify the element that replaces hydrogen from acids but cannot replace tin from its compounds.

3. According to Table 8-3, what is the most-active transition metal?

Answer

1. a. no

b. no

c. yes;
$2Cd(s) + 2HBr(aq) \longrightarrow 2CdBr(aq) + H_2(g)$

d. yes;
$Mg(s) + 2H_2O(g) \longrightarrow Mg(OH)_2(aq) + H_2(g)$

2. Pb

3. Mn

SECTION REVIEW

1. How is the activity series useful in predicting chemical behavior?

2. Based on the activity series, predict whether each of the following possible reactions listed will occur:
a. $Ni(s) + H_2O(l) \longrightarrow$ _____
b. $Br_2(l) + KI(aq) \longrightarrow$ _____
c. $Au(s) + HCl(aq) \longrightarrow$ _____
d. $Cd(s) + HCl(aq) \longrightarrow$ _____
e. $Mg(s) + Co(NO_3)_2(aq) \longrightarrow$ _____

3. For each of the reactions in item 2 that will occur, write the products and balance the equation.

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Acid Water—A Hidden Menace

When purchasing a home with its own well, it is common practice to have the water in the well tested. Usually, the purpose of the tests is to indicate the presence of disease-causing microorganisms. Rarely is the water's acidity measured.

Many people are unaware of their water's pH value (see Chapter 16) until they are confronted with such phenomena as a blue ring materializing around a porcelain sink drain, a water heater suddenly giving out, or tropical fish that keep dying. Each of these events could be traced to acidic water, which can also be a cause of lead poisoning.

The possibility of lead poisoning from home water supplies has gone largely unreported. Many older homes still have lead pipes in their plumbing, while most modern homes use copper piping. All pipe joints, however, are sealed with lead solder. Highly acidic water can leach out both the lead from the solder joints and copper from the pipes themselves, which turns the sink drain blue. In addition, people who are in the habit of filling their kettles in the morning without letting the tap run awhile first could be adding a number of unwanted chemicals to their tea or coffee.

Lead poisoning is of particular concern in young children. The absorption rate of lead in the intestinal tract of a child is much higher than that of an adult, and lead poisoning can permanently impair a child's rapidly growing nervous system. The good news is that lead poisoning and other effects of acidic water in the home can be easily prevented. Here's what you can do about it:

1. Monitor the pH of your water on a regular basis, especially if you have well water. This can easily be done with pH test kits (see photograph) that are sold in hardware or pet stores—many tropical fish are intolerant of water with a pH that is either too high (basic) or too low (acidic). The pH of most municipal water supplies should already be regulated, but it doesn't hurt to check.
2. In the morning, let your water tap run for about half a minute before you fill your kettle or drink the water. If the water is acidic, the first flush of water will have the highest concentration of lead and copper ions.
3. Installing an alkali-injection pump is a low-cost, low-maintenance solution that can save your plumbing and lessen the risk of lead poisoning from your own water supply. The pump injects a small amount of an alkali (usually potassium carbonate or sodium carbonate) in your water-holding tank each time you activate your well's pump. This effectively neutralizes the acidity of your water. The reaction below shows the neutralizing effect of potassium carbonate on well water that has been made acidic by acid rain.

$$K_2CO_3(aq) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + CO_2(g) + H_2O(l)$$

The pH of your home's water supply can be easily monitored using a test kit like the one shown here.

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CHAPTER 8 REVIEW

CHAPTER SUMMARY

8-1

- Five observations that suggest a chemical reaction is taking place are the evolution of heat or light, the production of gas, a change in color, and the formation of a precipitate.
- A balanced chemical equation represents, with symbols and formulas, the identities and relative amounts of reactants and products in a chemical reaction.

Vocabulary

chemical equation (241)
coefficient (243)
formula equation (244)
precipitate (242)
reversible reaction (246)
word equation (243)

8-2

- Synthesis reactions are represented by the general equation $A + X \longrightarrow AX$.
- Decomposition reactions are represented by the general equation $AX \longrightarrow A + X$.
- Single-replacement reactions are represented by the general equations $A + BX \longrightarrow AX + B$ and $Y + BX \longrightarrow BY + X$.
- Double-replacement reactions are represented by the general equation $AX + BY \longrightarrow AY + BX$.

Vocabulary

combustion reaction (263)
composition reaction (256)
decomposition reaction (259)
displacement reaction (261)
double-replacement reaction (262)
electrolysis (259)
single-replacement reaction (261)
synthesis reaction (256)

8-3

- Activity series list the elements in order of their chemical reactivity and are useful in predicting whether a chemical reaction will occur.
- Chemists determine activity series through experiments.

Vocabulary

activity series (265)

REVIEWING CONCEPTS

1. List four observations that indicate that a chemical reaction may be taking place. (8-1)
2. List the three requirements for a correctly written chemical equation. (8-1)
3. a. What is meant by the term *coefficient* in relation to a chemical equation?
   b. How does the presence of a coefficient affect the number of atoms of each type in the formula that it precedes? (8-1)
4. Give an example of a word equation, a formula equation, and a chemical equation. (8-1)
5. What quantitative information is revealed by a chemical equation? (8-1)
6. What limitations are associated with the use of both word and formula equations? (8-1)
7. Define each of the following:
   a. aqueous solution
   b. catalyst
   c. reversible reaction (8-1)
8. Write formulas for each of the following compounds:
   a. potassium hydroxide
   b. calcium nitrate
   c. sodium carbonate
   d. carbon tetrachloride
   e. magnesium bromide
   f. sulfur dioxide
   g. ammonium sulfate (8-1)

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9. What four guidelines are useful in balancing an equation? (8-1)

10. How many atoms of each type are represented in each of the following?
a. $3N_2$
b. $2H_2O$
c. $4HNO_3$
d. $2Ca(OH)_2$
e. $3Ba(ClO_3)_2$
f. $5Fe(NO_3)_2$
g. $4Mg_3(PO_4)_2$
h. $2(NH_4)_2SO_4$
i. $6Al_2(SeO_4)_3$
j. $4C_3H_8$ (8-1)

11. Define and give general equations for the five basic types of chemical reactions introduced in Chapter 8. (8-2)

12. How are most decomposition reactions initiated? (8-2)

13. What is electrolysis? (8-2)

14. a. In what environment do many single-replacement reactions commonly occur?
b. In general, how do single-replacement reactions compare with synthesis and decomposition reactions in terms of the amount of energy involved? (8-2)

15. a. What is meant by the *activity* of an element?
b. How does this description differ for metals and nonmetals? (8-3)

16. a. What is an activity series of elements?
b. What is the basis for the ordering of the elements in the activity series? (8-3)

17. a. What is the chemical principle upon which the activity series of metals is based?
b. What is the significance of the distance between two metals in the activity series? (8-3)

PROBLEMS

Chemical Equations

18. Write the chemical equation that relates to each of the following word equations. Include symbols for physical states in the equation. (Hint: See Sample Problem 8-1.)
a. solid zinc sulfide + oxygen gas ⟶ solid zinc oxide + sulfur dioxide gas
b. hydrochloric acid + aqueous magnesium hydroxide ⟶ aqueous magnesium chloride + water
c. nitric acid + aqueous calcium hydroxide ⟶ aqueous calcium nitrate + water

19. Translate each of the following chemical equations into a sentence. (Hint: See Sample Problem 8-2.)
a. $2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$
b. $CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$
c. $AgNO_3(aq) + KI(aq) \longrightarrow AgI(s) + KNO_3(aq)$

20. Balance each of the following:
a. $H_2 + Cl_2 \longrightarrow HCl$
b. $Al + Fe_2O_3 \longrightarrow Al_2O_3 + Fe$
c. $Pb(CH_3COO)_2 + H_2S \longrightarrow PbS + CH_3COOH$

21. The following equations are incorrect in some way. Identify and correct each error, and then balance each equation.
a. $Li + O_2 \longrightarrow LiO_2$
b. $H_2 + Cl_2 \longrightarrow H_2Cl_2$
c. $MgCO_3 \longrightarrow MgO_2 + CO_2$
d. $NaI + Cl_2 \longrightarrow NaCl + I$

22. Write chemical equations for each of the following sentences:
a. Aluminum reacts with oxygen to produce aluminum oxide.
b. Phosphoric acid, H_3PO_4, is produced through the reaction between tetraphosphorus decoxide and water.
c. Iron(III) oxide reacts with carbon monoxide to produce iron and carbon dioxide.

23. Carbon tetrachloride is used as an intermediate chemical in the manufacture of other chemicals. It is prepared in liquid form by reacting chlorine gas with methane gas. Hydrogen chloride gas is also formed in this reaction. Write the balanced chemical equation for the production of carbon tetrachloride. (Hint: See Sample Problems 8-3 and 8-4.)

24. For each of the following synthesis reactions, identify the missing reactant(s) or product(s), and then balance the resulting equation:
a. $Mg + \_\_\_\_\_ \longrightarrow MgO$
b. $\_\_\_\_\_ + O_2 \longrightarrow Fe_2O_3$
c. $Li + Cl_2 \longrightarrow \_\_\_\_\_$
d. $Ca + \_\_\_\_\_ \longrightarrow CaI_2$

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Types of Chemical Reactions

25. Complete the following synthesis reactions by writing both word and chemical equations for each:
a. sodium + oxygen ⟶ _____
b. magnesium + fluorine ⟶ _____

26. Complete and balance the equation for each of the following decomposition reactions:
a. $HgO \xrightarrow{\Delta}$
b. $H_2O(l) \xrightarrow{\text{electricity}}$
c. $Ag_2O \xrightarrow{\Delta}$
d. $CuCl_2 \xrightarrow{\text{electricity}}$

27. Complete and balance the equations for each of the following single-replacement reactions:
a. $Zn + Pb(NO_3)_2 \longrightarrow$ _____
b. $Al + Hg(CH_3COO)_2 \longrightarrow$ _____
c. $Al + NiSO_4 \longrightarrow$ _____
d. $Na + H_2O \longrightarrow$ _____

28. Complete and balance the equations for the following double-replacement reactions:
a. $AgNO_3(aq) + NaCl(aq) \longrightarrow$ _____
b. $Mg(NO_3)_2(aq) + KOH(aq) \longrightarrow$ _____
c. $LiOH(aq) + Fe(NO_3)_3(aq) \longrightarrow$ _____

29. Complete and balance the equation for each of the following combustion reactions:
a. $CH_4 + O_2 \longrightarrow$ _____
b. $C_3H_6 + O_2 \longrightarrow$ _____
c. $C_5H_{12} + O_2 \longrightarrow$ _____

30. Write and balance each of the following equations, and then identify each by type:
a. hydrogen + iodine ⟶ hydrogen iodide
b. lithium + hydrochloric acid ⟶ lithium chloride + hydrogen
c. sodium carbonate ⟶ sodium oxide + carbon dioxide
d. mercury(II) oxide ⟶ mercury + oxygen
e. magnesium hydroxide ⟶ magnesium oxide + water

31. Identify the compound that could undergo decomposition to produce the following products, and then balance the final equation:
a. magnesium oxide and water
b. lead(II) oxide and water
c. lithium chloride and oxygen
d. barium chloride and oxygen
e. nickel chloride and oxygen

32. In each of the following combustion reactions, identify the missing reactant(s), product(s), or both, and then balance the resulting equation:
a. $C_3H_8 +$ _____ ⟶ _____ $+ H_2O$
b. _____ $+ 8O_2 \longrightarrow 5CO_2 + 6H_2O$
c. $C_2H_5OH +$ _____ ⟶ _____ + _____

33. Complete and balance each of the following reactions observed to occur, and then identify each by type:
a. zinc + sulfur ⟶ _____
b. calcium + sodium nitrate ⟶ _____
c. silver nitrate + potassium iodide ⟶ _____
d. sodium iodide $\xrightarrow{\Delta}$ _____
e. toluene, C_7H_8 + oxygen ⟶ _____
f. nonane, C_9H_{20} + oxygen ⟶ _____

Activity Series

34. Based on the activity series of metals and halogens, which element within each pair is more likely to replace the other in a compound?
a. K and Na
b. Al and Ni
c. Bi and Cr
d. Cl and F
e. Au and Ag
f. Cl and I
g. Fe and Sr
h. I and F

35. Using the activity series in Table 8-3 on page 266, predict whether each of the possible reactions listed below will occur. For the reactions that will occur, write the products and balance the equation.
a. $Ni(s) + CuCl_2(aq) \longrightarrow$ _____
b. $Zn(s) + Pb(NO_3)_2(aq) \longrightarrow$ _____
c. $Cl_2(g) + KI(aq) \longrightarrow$ _____
d. $Cu(s) + FeSO_4(aq) \longrightarrow$ _____
e. $Ba(s) + H_2O(l) \longrightarrow$ _____

36. Use the activity series to predict whether each of the following synthesis reactions will occur, and write the chemical equations for those predicted to occur:
a. $Ca(s) + O_2(g) \longrightarrow$ _____
b. $Ni(s) + O_2(g) \longrightarrow$ _____
c. $Au(s) + O_2(g) \longrightarrow$ _____

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MIXED REVIEW

37. Ammonia reacts with oxygen to yield nitrogen and water.

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$$

Given this chemical equation, as well as the number of moles of the reactant or product indicated below, determine the number of moles of all remaining reactants and products.

a. 3.0 mol O_2
b. 8.0 mol NH_3
c. 1.0 mol N_2
d. 0.40 mol H_2O

38. Complete the following synthesis reactions by writing both the word and chemical equation for each:

a. potassium + chlorine ⟶ _____
b. hydrogen + iodine ⟶ _____
c. magnesium + oxygen ⟶ _____

39. Use the activity series to predict which metal, Sn, Mn, or Pt, would be the best choice as a container for an acid.

40. Aqueous sodium hydroxide is produced commercially by the electrolysis of aqueous sodium chloride. Hydrogen and chlorine gases are also produced. Write the balanced chemical equation for the production of sodium hydroxide. Include the physical states of the reactants and products.

41. Balance each of the following:

a. $Ca(OH)_2 + (NH_4)_2SO_4 \longrightarrow CaSO_4 + NH_3 + H_2O$
b. $C_2H_6 + O_2 \longrightarrow CO_2 + H_2O$
c. $Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$
d. $Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$

42. Use the activity series to predict whether each of the following reactions will occur, and write the balanced chemical equations for those predicted to occur:

a. $Al(s) + O_2(g) \longrightarrow$ _____
b. $Pb(s) + ZnCl_2(s) \longrightarrow$ _____
c. $Rb(s) + Zn(NO_3)_2(aq) \longrightarrow$ _____

43. Complete and balance the equations for the following reactions, and identify the type of reaction each represents:

a. $(NH_4)_2S(aq) + ZnCl_2(aq) \longrightarrow$ _____ + $ZnS(s)$
b. $Al(s) + Pb(NO_3)_2(aq) \longrightarrow$ _____
c. $Ba(s) + H_2O(l) \longrightarrow$ _____
d. $Cl_2(g) + KBr(aq) \longrightarrow$
e. $NH_3(g) + O_2(g) \xrightarrow{Pt} NO(g) + H_2O(l)$
f. $H_2O(l) \longrightarrow H_2(g) + O_2(g)$

44. Write and balance each of the following equations, and then identify each by type:

a. copper + chlorine ⟶ copper(II) chloride
b. calcium chlorate ⟶ calcium chloride + oxygen
c. lithium + water ⟶ lithium hydroxide + hydrogen
d. lead(II) carbonate ⟶ lead(II) oxide + carbon dioxide

45. How many moles of HCl can be made from 6.15 mol of H_2 and an excess of Cl_2?

46. What product is missing in the following equation?

$$MgO + 2HCl \longrightarrow MgCl_2 + \text{_____}$$

47. Balance the following equations:

a. $Pb(NO_3)_2(aq) + NaOH(aq) \longrightarrow Pb(OH)_2(s) + NaNO_3(aq)$
b. $C_{12}H_{22}O_{11}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$
c. $Al(OH)_3(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + H_2O(l)$

48. Translate the following word equations into balanced chemical equations:

a. silver nitrate + potassium iodide ⟶ silver iodide + potassium nitrate
b. nitrogen dioxide + water ⟶ nitric acid + nitrogen monoxide
c. silicon tetrachloride + water ⟶ silicon dioxide + hydrochloric acid

CRITICAL THINKING

49. Inferring Relationships Activity series are prepared by comparing single-displacement reactions between metals. Based on observations, the metals can be ranked by their ability to react. However, reactivity can be explained by the ease with which atoms of metals lose electrons. Using information from the activity series, identify the locations in the periodic table of the most-reactive metals and the

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least-reactive metals. Based on your knowledge of electron configurations and periodic trends, infer possible explanations for their reactivity and position in the periodic table.

50. Analyzing Results Formulate an activity series for the hypothetical elements A, J, Q, and Z using the reaction information provided.

$$A + ZX \longrightarrow AX + Z$$
$$J + ZX \longrightarrow \text{no reaction}$$
$$Q + AX \longrightarrow QX + A$$

HANDBOOK SEARCH

51. Find the common-reactions section for Group 1 metals in the *Elements Handbook*. Use this information to answer the following:
- a. Write a balanced chemical equation for the formation of rubidium hydroxide from rubidum oxide.
- b. Write a balanced chemical equation for the formation of cesium iodide.
- c. Classify the reactions you wrote in (a) and (b).
- d. Write word equations for the reactions you wrote in (a) and (b).

52. Find the common-reactions section for Group 13 in the *Elements Handbook*. Use this information to answer the following:
- a. Write a balanced chemical equation for the formation of gallium bromide prepared from hydrobromic acid.
- b. Write a balanced chemical equation for the formation of gallium oxide.
- c. Classify the reactions you wrote in (a) and (b).
- d. Write word equations for the reactions you wrote in (a) and (b).

53. Find the common-reactions section for Group 16 in the *Elements Handbook*. Use this information to answer the following:
- a. Write a balanced chemical equation for the formation of selenium trioxide.
- b. Write a balanced chemical equation for the formation of tellurium iodide.
- c. Classify the reactions you wrote in (a) and (b).
- d. Write word equations for the reactions you wrote in (a) and (b).

RESEARCH & WRITING

54. Trace the evolution of municipal water fluoridation. What advantages and disadvantages are associated with this practice?

55. Research how a soda-acid fire extinguisher works, and write the chemical equation for the reaction. Check your house and other structures for different types of fire extinguishers, and ask your local fire department to verify the effectiveness of each type of extinguisher.

ALTERNATIVE ASSESSMENT

56. Performance Assessment For one day, record situations that show evidence of a chemical change. Identify the reactants and the products, and determine whether there is proof of a chemical reaction. Classify each of the chemical reactions according to the common reaction types discussed in the chapter.

57. Design a set of experiments that will enable you to create an activity series for the elements composing the following metals and solutions:
- a. aluminum and aluminum chloride
- b. chromium and chromium(III) chloride
- c. iron and iron(II) chloride
- d. magnesium and magnesium chloride

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CHAPTER 9

Stoichiometry

Stoichiometry *comes from the Greek words* stoicheion, *meaning "element," and* metron, *meaning "measure."*

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Introduction to Stoichiometry

SECTION 9-1

OBJECTIVES

- Define *stoichiometry.*
- Describe the importance of the *mole ratio* in stoichiometric calculations.
- Write a mole ratio relating two substances in a chemical equation.

Much of our knowledge of chemistry is based on the careful quantitative analysis of substances involved in chemical reactions. **Composition stoichiometry** (which you studied in Chapter 3) *deals with the mass relationships of elements in compounds*. **Reaction stoichiometry** *involves the mass relationships between reactants and products in a chemical reaction.* Reaction stoichiometry is the subject of this chapter and it is based on chemical equations and the law of conservation of matter. All reaction-stoichiometry calculations start with a balanced chemical equation. This equation gives the relative numbers of moles of reactants and products.

Reaction-Stoichiometry Problems

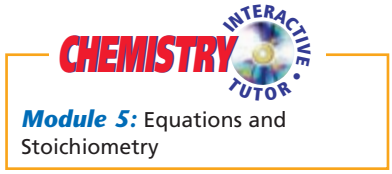
The reaction-stoichiometry problems in this chapter can be classified according to the information *given* in the problem and the information you are expected to find, the *unknown*. The *given* and the *unknown* may both be reactants, they may both be products, or one may be a reactant and the other a product. The masses are generally expressed in grams, but you will encounter both large-scale and microscale problems with other mass units, such as kg or mg. Stoichiometric problems are solved by using ratios from the balanced equation to convert the given quantity using the methods described here.

Problem Type 1: *Given* and *unknown* quantities are amounts in moles.
When you are given the amount of a substance in moles and asked to calculate the amount in moles of another substance in the chemical reaction, the general plan is

$$\text{amount of } \textit{given} \text{ substance (in mol)} \longrightarrow \text{amount of } \textit{unknown} \text{ substance (in mol)}$$

Problem Type 2: *Given* is an amount in moles and the *unknown* is a mass that is often expressed in grams.
When you are given the amount in moles of one substance and asked to calculate the mass of another substance in the chemical reaction, the general plan is

$$\text{amount of } \textit{given} \text{ substance (in mol)} \longrightarrow \text{amount of } \textit{unknown} \text{ substance (in mol)} \longrightarrow \text{mass of } \textit{unknown} \text{ substance (in g)}$$



Module 5: Equations and Stoichiometry

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Problem Type 3: *Given* is a mass in grams and the *unknown* is an amount in moles.

When you are given the mass of one substance and asked to calculate the amount in moles of another substance in the chemical reaction, the general plan is

mass of *given* substance (in g) ⟶ amount of *given* substance (in mol) ⟶ amount of *unknown* substance (in mol)

Problem Type 4: *Given* is a mass in grams and the *unknown* is a mass in grams.

When you are given the mass of one substance and asked to calculate the mass of another substance in the chemical reaction, the general plan is

mass of *given* substance (in g) ⟶ amount of *given* substance (in mol) ⟶ amount of *unknown* substance (in mol) ⟶ mass of *unknown* substance (in g)

Mole Ratio

Solving any reaction-stoichiometry problem requires the use of a mole ratio to convert from moles or grams of one substance in a reaction to moles or grams of another substance. *A* **mole ratio** *is a conversion factor that relates the amounts in moles of any two substances involved in a chemical reaction.* This information is obtained directly from the balanced chemical equation. Consider, for example, the chemical equation for the electrolysis of aluminum oxide to produce aluminum and oxygen.

$$2Al_2O_3(l) \longrightarrow 4Al(s) + 3O_2(g)$$

Recall from Chapter 8 that the coefficients in a chemical equation satisfy the law of conservation of matter and represent the relative amounts in moles of reactants and products. Therefore, 2 mol of aluminum oxide decompose to produce 4 mol of aluminum and 3 mol of oxygen gas. These relationships can be expressed in the following mole ratios.

$$\frac{2\ \text{mol}\ Al_2O_3}{4\ \text{mol}\ Al} \quad \text{or} \quad \frac{4\ \text{mol}\ Al}{2\ \text{mol}\ Al_2O_3}$$

$$\frac{2\ \text{mol}\ Al_2O_3}{3\ \text{mol}\ O_2} \quad \text{or} \quad \frac{3\ \text{mol}\ O_2}{2\ \text{mol}\ Al_2O_3}$$

$$\frac{4\ \text{mol}\ Al}{3\ \text{mol}\ O_2} \quad \text{or} \quad \frac{3\ \text{mol}\ O_2}{4\ \text{mol}\ Al}$$

For the decomposition of aluminum oxide, the appropriate mole ratio would be used as a conversion factor to convert a given amount in moles of one substance to the corresponding amount in moles of another

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substance. To determine the amount in moles of aluminum that can be produced from 13.0 mol of aluminum oxide, the mole ratio needed is that of Al to Al_2O_3.

$$13.0 \text{ mol } Al_2O_3 \times \frac{4 \text{ mol Al}}{2 \text{ mol } Al_2O_3} = 26.0 \text{ mol Al}$$

Mole ratios are exact, so they do not limit the number of significant figures in a calculation. The number of significant figures in the answer is therefore determined only by the number of significant figures of any measured quantities in a particular problem.

Molar Mass

Recall from Chapter 7 that the molar mass is the mass, in grams, of one mole of a substance. The molar mass is the conversion factor that relates the mass of a substance to the amount in moles of that substance. To solve reaction-stoichiometry problems, you will need to determine molar masses using the periodic table.

Returning to the previous example, the decomposition of aluminum oxide, the rounded masses from the periodic table are the following.

$$Al_2O_3 = 101.96 \text{ g/mol} \qquad O_2 = 32.00 \text{ g/mol} \qquad Al = 26.98 \text{ g/mol}$$

These molar masses can be expressed by the following conversion factors.

$$\frac{101.96 \text{ g } Al_2O_3}{\text{mol } Al_2O_3} \text{ or } \frac{1 \text{ mol } Al_2O_3}{101.96 \text{ g } Al_2O_3}$$

$$\frac{26.98 \text{ g Al}}{\text{mol Al}} \text{ or } \frac{1 \text{ mol Al}}{26.98 \text{ g Al}}$$

$$\frac{32.00 \text{ g } O_2}{\text{mol } O_2} \text{ or } \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2}$$

To find the number of grams of aluminum equivalent to 26.0 mol of aluminum, the calculation would be as follows.

$$26.0 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{\text{mol Al}} = 701 \text{ g Al}$$

SECTION REVIEW

1. What is stoichiometry?
2. How is a mole ratio from a reaction used in stoichiometric problems?
3. For each of the following chemical equations, write all possible mole ratios.
   a. $2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
   b. $4NH_3(g) + 6NO(g) \longrightarrow 5N_2(g) + 6H_2O(l)$
   c. $2Al(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$

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The Case of Combustion

HISTORICAL PERSPECTIVE

People throughout history have transformed substances by burning them in the air. Yet at the dawn of the scientific revolution, very little was known about the process of combustion. In attempting to explain this common phenomenon, chemists of the eighteenth century developed one of the first universally accepted theories in their field. But, as one man would show, scientific theories do not always stand the test of time.

Changing Attitudes

Shunning the ancient Greek approach of logical argument based on untested premises, investigators of the seventeenth century began to understand the laws of nature by observing, measuring, and performing experiments on the world around them. However, this scientific method was incorporated into chemistry slowly. Though early chemists experimented extensively, most disregarded the importance of measurement, an oversight that set chemistry on the wrong path for nearly a century.

A Flawed Theory

By 1700, combustion was assumed to be the decomposition of a material into simpler substances. People saw burning substances emitting heat, smoke, and light. To account for it, a theory was proposed that combustion depended on the emission of a substance called phlogiston, which appeared as a combination of heat and light while the material was burning but which couldn't be detected beforehand.

Antoine-Laurent Lavoisier and his wife, Marie-Anne Pierrette Lavoisier, who assisted him. One of her important roles was to translate the papers of important scientists for her husband.

The Metropolitan Museum of Art, Purchase, Mr. and Mrs. Charles Wrightsman Gift, in honor of Everett Fahy, 1977. (1977.10) Copyright © 1989 By The Metropolitan Museum of Art.

The phlogiston theory was used to explain many chemical observations of the day. For example, a lit candle under a glass jar burned until the surrounding air became saturated with phlogiston, at which time the flame died because the air inside could not absorb more phlogiston.

A New Phase of Study

By the 1770s, the phlogiston theory had gained universal acceptance. At that time, chemists also began to experiment with air, which was generally believed to be an element.

In 1772, when Daniel Rutherford found that a mouse kept in a closed container soon died, he explained the results based on the phlogiston theory. Like a burning candle, the mouse emitted phlogiston; when the air could hold no more phlogiston, the mouse died. Thus, Rutherford figured he had obtained "phlogisticated air."

A couple of years later, Joseph Priestley found that when he heated mercury in air, he obtained a reddish powder, which he assumed to be mercury devoid of phlogiston. But when he decided to heat the powder, he recorded an unexpected result:

> *I endeavored to extract air from [the powder by heating it]; and I presently found that*

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> *. . . air was expelled from it readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that water was not imbibed by it. But what surprised me more . . . was, that a candle in this air burned . . . remarkably . . .*

Following the phlogiston theory, he believed this gas that supports combustion to be "dephlogisticated air."

Nice Try, But . . .

Antoine Laurent Lavoisier was a meticulous scientist. He realized that Rutherford and Priestley had carefully observed and described their experiments but had not weighed anything. Unlike his colleagues, Lavoisier knew the importance of using a balance:

> *. . . making experiments . . . is founded on this principle . . . always suppose an exact equality or equation between the principles [masses] of the body examined and those of the products of its analysis.*

Applying this rule, which would become known as the law of conservation of mass, Lavoisier endeavored to explain the results of Rutherford and Priestley.

He put some tin in a closed vessel and weighed the entire system. He then burned the tin. When he opened the vessel, air rushed into it, as if something had been *removed* from the air during combustion. He then weighed the burnt metal and observed a weight increase relative to the original tin. Curiously, this increase equaled the weight of the air that had rushed into the vessel. To Lavoisier, this did not support the idea of phlogiston escaping the burning material. Instead, it indicated that during combustion a portion of air was depleted.

After obtaining similar results using a variety of substances, Lavoisier concluded that air was not an element at all but a mixture composed principally of two gases, Priestley's "dephlogisticated air" (which Lavoisier renamed oxygen) and Rutherford's "phlogisticated air" (which was mostly nitrogen, with traces of other nonflammable atmospheric gases). When a substance burned, it chemically combined with oxygen, resulting in a product Lavoisier named an "oxide." Lavoisier's theory of combustion persists today. He used the name *oxygen* because he thought that all acids contained oxygen. *Oxygen* means "acid former."

The Father of Chemistry

By emphasizing the importance of quantitative analysis, Lavoisier helped establish chemistry as a science. His work on combustion laid to rest the theories of phlogiston and that air is an element. He also explained why hydrogen burned in oxygen to form water, or hydrogen oxide. He later published one of the first chemistry textbooks, which established a common naming system of compounds and elements and helped unify chemistry worldwide, earning him the reputation as the father of chemistry.

internetconnect
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TOPIC: Lavoisier
GO TO: www.scilinks.org
***sci*LINKS CODE:** HC2091

TABLE OF SIMPLE SUBSTANCES.

Simple fubftances belonging to all the kingdoms of nature, which may be confidered as the elements of bodies.

New Names.	*Correfpondent old Names.*
Light	*Light.*
Caloric	*Heat.* *Principle or element of heat.* *Fire. Igneous fluid.* *Matter of fire and of heat.*
Oxygen	*Dephlogifticated air.* *Empyreal air.* *Vital air, or* *Bafe of vital air.*
Azote	*Phlogifticated air or gas.* *Mephitis, or its bafe.*
Hydrogen	*Inflammable air or gas,* *or the bafe of inflammable air.*

Lavoisier's concept of simple substances as published in his book Elements of Chemistry *in 1789.*

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SECTION 9-2

OBJECTIVES

- Calculate the amount in moles of a reactant or product from the amount in moles of a different reactant or product.
- Calculate the mass of a reactant or product from the amount in moles of a different reactant or product.
- Calculate the amount in moles of a reactant or product from the mass of a different reactant or product.
- Calculate the mass of a reactant or product from the mass of a different reactant or product.

Ideal Stoichiometric Calculations

The chemical equation plays a very important part in all stoichiometric calculations because the mole ratio is obtained directly from it. Solving any reaction-stoichiometry problem must begin with a balanced equation.

Chemical equations help us make predictions about chemical reactions without having to run the reactions in the laboratory. The reaction-stoichiometry calculations described in this chapter are theoretical. They tell us the amounts of reactants and products for a given chemical reaction under *ideal conditions,* in which all reactants are completely converted into products. However, ideal conditions are rarely met in the laboratory or in industry. Yet, theoretical stoichiometric calculations serve the very important function of showing the maximum amount of product that could be obtained before a reaction is run in the laboratory.

Solving stoichiometric problems requires practice. These problems are extensions of the composition-stoichiometry problems you solved in Chapters 3 and 7. Practice by working the sample problems in the rest of this chapter. Using a logical, systematic approach will help you successfully solve these problems.

Conversions of Quantities in Moles

In these stoichiometric problems, you are asked to calculate the amount in moles of one substance that will react with or be produced from the given amount in moles of another substance. The plan for a simple mole conversion problem is

$$\text{amount of } \textit{given} \text{ substance (in mol)} \longrightarrow \text{amount of } \textit{unknown} \text{ substance (in mol)}$$

This plan requires one conversion factor—the stoichiometric mole ratio of the *unknown* substance to the *given* substance from the balanced equation. To solve this type of problem, simply multiply the *known* quantity by the appropriate conversion factor.

$$\textit{given} \text{ quantity} \times \text{conversion factor} = \textit{unknown} \text{ quantity}$$

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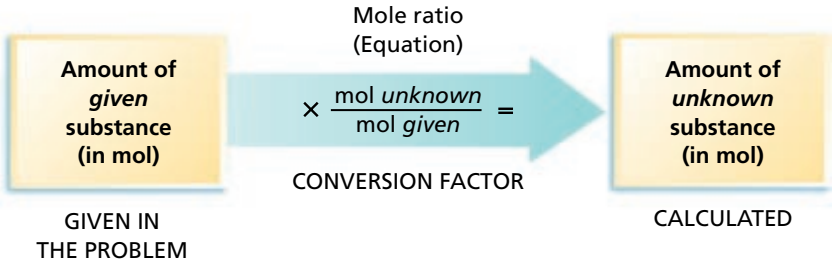

FIGURE 9-1 This is a solution plan for problems in which the given and unknown quantities are expressed in moles.

SAMPLE PROBLEM 9-1

In a spacecraft, the carbon dioxide exhaled by astronauts can be removed by its reaction with lithium hydroxide, LiOH, according to the following chemical equation.

$$CO_2(g) + 2LiOH(s) \longrightarrow Li_2CO_3(s) + H_2O(l)$$

How many moles of lithium hydroxide are required to react with 20 mol of CO_2, the average amount exhaled by a person each day?

SOLUTION

1 *ANALYZE*

Given: amount of CO_2 = 20 mol
Unknown: amount of LiOH in moles

2 *PLAN*

amount of CO_2 (in mol) ⟶ amount of LiOH (in mol)

This problem requires one conversion factor—the mole ratio of LiOH to CO_2. The mole ratio is obtained from the balanced chemical equation. Because you are given moles of CO_2, select a mole ratio that will give you mol LiOH in your final answer. The correct ratio is the following.

$$\frac{\text{mol LiOH}}{\text{mol } CO_2}$$

This ratio gives the units mol LiOH in the answer.

$$\text{mol } CO_2 \times \overset{\text{mol ratio}}{\frac{\text{mol LiOH}}{\text{mol } CO_2}} = \text{mol LiOH}$$

3 *COMPUTE*

Substitute the values in the equation in step 2, and compute the answer.

$$20 \text{ mol } \cancel{CO_2} \times \frac{2 \text{ mol LiOH}}{1 \text{ mol } \cancel{CO_2}} = 40 \text{ mol LiOH}$$

4 *EVALUATE*

The answer is rounded correctly to one significant figure to match that in the factor 20 mol CO_2, and the units cancel to leave mol LiOH, which is the unknown. The equation shows that twice the amount in moles of LiOH react with CO_2. Therefore, the answer should be greater than 20.

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PRACTICE

1. Ammonia, NH_3, is widely used as a fertilizer and in many household cleaners. How many moles of ammonia are produced when 6 mol of hydrogen gas react with an excess of nitrogen gas?

Answer
4 mol NH_3

2. The decomposition of potassium chlorate, $KClO_3$, is used as a source of oxygen in the laboratory. How many moles of potassium chlorate are needed to produce 15 mol of oxygen?

Answer
10. mol $KClO_3$

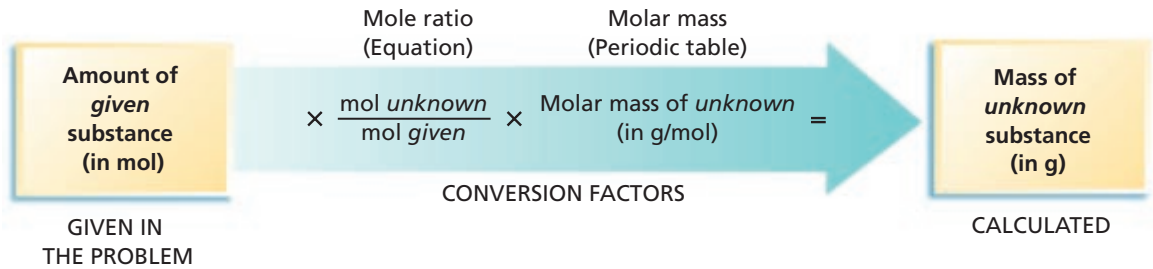
Conversions of Amounts in Moles to Mass

In these stoichiometric calculations, you are asked to calculate the mass (usually in grams) of a substance that will react with or be produced from a given amount in moles of a second substance. The plan for these mole to gram conversions is

amount of *given* substance (in mol) ⟶ amount of *unknown* substance (in mol) ⟶ mass of *unknown* substance (in g)

This plan requires two conversion factors—the mole ratio of the *unknown* substance to the *given* substance and the molar mass of the *unknown* substance for the mass conversion. To solve this kind of problem, you simply multiply the known quantity, which is the amount in moles, by the appropriate conversion factors.

FIGURE 9-2 This is a solution plan for problems in which the given quantity is expressed in moles and the unknown quantity is expressed in grams.


Mole ratio
(Equation)
Molar mass
(Periodic table)
Amount of *given* substance (in mol)
× mol *unknown* / mol *given* × Molar mass of *unknown* (in g/mol) =
Mass of *unknown* substance (in g)
CONVERSION FACTORS
GIVEN IN THE PROBLEM
CALCULATED

SAMPLE PROBLEM 9-2

In photosynthesis, plants use energy from the sun to produce glucose, $C_6H_{12}O_6$, and oxygen from the reaction of carbon dioxide and water. What mass, in grams, of glucose is produced when 3.00 mol of water react with carbon dioxide?

SOLUTION

1 *ANALYZE*

Given: amount of H_2O = 3.00 mol
Unknown: mass of $C_6H_{12}O_6$ produced (in g)

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2 PLAN

You must start with a balanced equation.

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Given the amount in mol of H_2O, you need to get the mass of $C_6H_{12}O_6$ in grams. Two conversion factors are needed—the mole ratio of $C_6H_{12}O_6$ to H_2O and the molar mass of $C_6H_{12}O_6$.

$$\text{mol } H_2O \times \frac{\overset{\text{mol ratio}}{\text{mol } C_6H_{12}O_6}}{\text{mol } H_2O} \times \frac{\overset{\text{molar mass}}{\text{g } C_6H_{12}O_6}}{\text{mol } C_6H_{12}O_6} = \text{g } C_6H_{12}O_6$$

3 COMPUTE

Use the periodic table to compute the molar mass of $C_6H_{12}O_6$.

$$C_6H_{12}O_6 = 180.18 \text{ g/mol}$$

$$3.00 \cancel{\text{ mol } H_2O} \times \frac{1 \cancel{\text{ mol } C_6H_{12}O_6}}{6 \cancel{\text{ mol } H_2O}} \times \frac{180.18 \text{ g } C_6H_{12}O_6}{1 \cancel{\text{ mol } C_6H_{12}O_6}} = 90.1 \text{ g } C_6H_{12}O_6$$

4 EVALUATE

The answer is correctly rounded to three significant figures, to match those in 3.00 mol H_2O. The units cancel in the problem, leaving g $C_6H_{12}O_6$ as the units for the answer, which matches the unknown. The answer is reasonable because it is one-half of 180.

SAMPLE PROBLEM 9-3

What mass of carbon dioxide, in grams, is needed to react with 3.00 mol of H_2O in the photosynthetic reaction described in Sample Problem 9-2?

SOLUTION

1 ANALYZE

Given: amount of H_2O = 3.00 mol
Unknown: mass of CO_2 in grams

2 PLAN

The chemical equation from Sample Problem 9-2 is

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g).$$

Two conversion factors are needed—the mole ratio of CO_2 to H_2O and the molar mass of CO_2.

$$\text{mol } H_2O \times \frac{\overset{\text{mol ratio}}{\text{mol } CO_2}}{\text{mol } H_2O} \times \frac{\overset{\text{molar mass}}{\text{g } CO_2}}{\text{mol } CO_2} = \text{g } CO_2$$

3 COMPUTE

Use the periodic table to compute the molar mass of CO_2.

$$CO_2 = 44.01 \text{ g/mol}$$

$$3.00 \cancel{\text{ mol } H_2O} \times \frac{6 \cancel{\text{ mol } CO_2}}{6 \cancel{\text{ mol } H_2O}} \times \frac{44.01 \text{ g } CO_2}{\cancel{\text{mol } CO_2}} = 132 \text{ g } CO_2$$

4 EVALUATE

The answer is rounded correctly to three significant figures to match those in 3.00 mol H_2O. The units cancel to leave g CO_2, which is the unknown. The answer is close to an estimate of 120, which is 3×40.

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PRACTICE

1. When magnesium burns in air, it combines with oxygen to form magnesium oxide according to the following equation.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

What mass in grams of magnesium oxide is produced from 2.00 mol of magnesium?

Answer
80.6 g MgO

2. What mass in grams of oxygen combines with 2.00 mol of magnesium in this same reaction?

Answer
32.0 g O_2

3. What mass of glucose can be produced from a photosynthesis reaction that occurs using 10 mol CO_2?

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

Answer
300 g $C_6H_{12}O_6$

Conversions of Mass to Amounts in Moles

In these stoichiometric calculations, you are asked to calculate the amount in moles of one substance that will react with or be produced from a given mass of another substance. In this type of problem you are starting with a mass (probably in grams) of some substance. The plan for this conversion is

mass of *given* substance (in g) ⟶ amount of *given* substance (in mol) ⟶ amount of *unknown* substance (in mol)

This route also requires two additional pieces of data: the molar mass of the *given* substance and the mole ratio. The molar mass is determined using masses from the periodic table. To convert the mass of a substance to moles we are using a factor which we will call the inverted molar mass. It is simply one over the molar mass. To solve this type of problem, simply multiply or divide the known quantity by the appropriate conversion factors as follows.

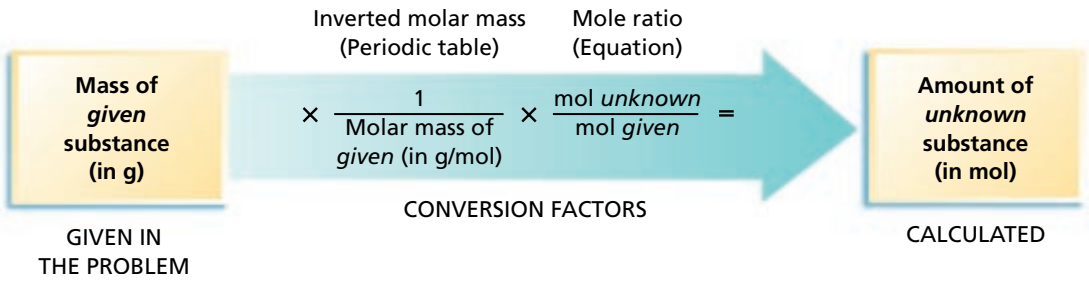
Inverted molar mass (Periodic table)
Mole ratio (Equation)
Mass of *given* substance (in g)
× 1 / Molar mass of *given* (in g/mol) × mol *unknown* / mol *given* =
Amount of *unknown* substance (in mol)
CONVERSION FACTORS
GIVEN IN THE PROBLEM
CALCULATED

FIGURE 9-3 This is a solution plan for problems in which the given quantity is expressed in grams and the unknown quantity is expressed in moles.

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SAMPLE PROBLEM 9-4

The first step in the industrial manufacture of nitric acid is the catalytic oxidation of ammonia.

$$NH_3(g) + O_2(g) \longrightarrow NO(g) + H_2O(g) \quad \text{(unbalanced)}$$

The reaction is run using 824 g of NH_3 and excess oxygen.
a. How many moles of NO are formed?
b. How many moles of H_2O are formed?

SOLUTION

1 ANALYZE

Given: mass of NH_3 = 824 g
Unknown: **a.** amount of NO produced (in mol)
b. amount of H_2O produced (in mol)

2 PLAN

First, write the balanced chemical equation.

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

Two conversion factors are needed to solve part (a)—the molar mass of NH_3 and the mole ratio of NO to NH_3. Part (b) starts with the same conversion factor as part (a), but then the mole ratio of H_2O to NH_3 is used to convert to the amount in moles of H_2O. The first conversion factor in each part is the inverted molar mass of NH_3.

$$\text{a. g } NH_3 \times \overbrace{\frac{1 \text{ mol } NH_3}{\text{g } NH_3}}^{\text{inverted molar mass}} \times \overbrace{\frac{\text{mol NO}}{\text{mol } NH_3}}^{\text{mol ratio}} = \text{mol NO}$$

$$\text{b. g } NH_3 \times \overbrace{\frac{1 \text{ mol } NH_3}{\text{g } NH_3}}^{\text{inverted molar mass}} \times \overbrace{\frac{\text{mol } H_2O}{\text{mol } NH_3}}^{\text{mol ratio}} = \text{mol } H_2O$$

3 COMPUTE

Use the periodic table to compute the molar mass of NH_3.

$$NH_3 = 17.04 \text{ g/mol}$$

$$\text{a. } 824 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.04 \text{ g } NH_3} \times \frac{4 \text{ mol NO}}{4 \text{ mol } NH_3} = 48.4 \text{ mol NO}$$

$$\text{b. } 824 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.04 \text{ g } NH_3} \times \frac{6 \text{ mol } H_2O}{4 \text{ mol } NH_3} = 72.6 \text{ mol } H_2O$$

4 EVALUATE

The answers are correctly given to three significant figures. The units cancel in the two problems to leave mol NO and mol H_2O, respectively, which are the unknowns.

PRACTICE

Oxygen was discovered by Joseph Priestley in 1774 when he heated mercury(II) oxide to decompose it to form its constituent elements.

1. How many moles of mercury(II) oxide, HgO, are needed to produce 125 g of oxygen, O_2?

Answer
7.81 mol HgO

2. How many moles of mercury are produced?

Answer
7.81 mol Hg

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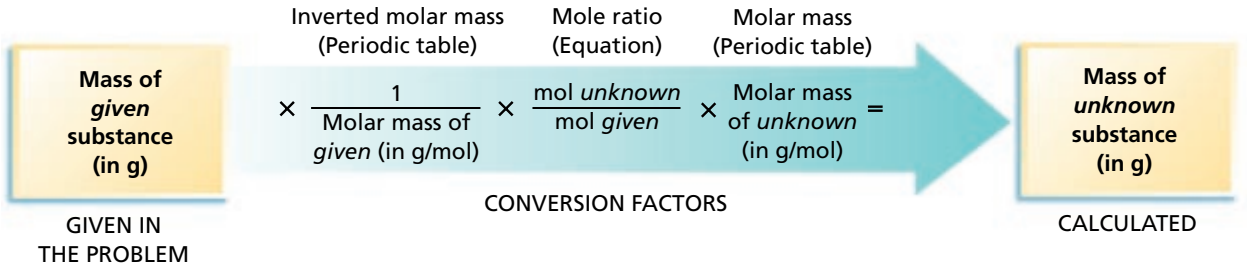
Inverted molar mass (Periodic table)
Mole ratio (Equation)
Molar mass (Periodic table)
Mass of *given* substance (in g)
× 1 / Molar mass of *given* (in g/mol)
× mol *unknown* / mol *given*
× Molar mass of *unknown* (in g/mol) =
Mass of *unknown* substance (in g)
CONVERSION FACTORS
GIVEN IN THE PROBLEM
CALCULATED

FIGURE 9-4 This is a solution plan for problems in which the given quantity is expressed in grams and the unknown quantity is also expressed in grams.

Mass-Mass Calculations

Mass-mass calculations are more practical than other mole calculations you have studied. You can never measure moles directly. You are generally required to calculate the amount in moles of a substance from its mass, which you can measure in the lab. Mass-mass problems can be viewed as the combination of the other types of problems. The plan for solving mass-mass problems is

mass of *given* substance (in g) ⟶ amount of *given* substance (in mol) ⟶ amount of *unknown* substance (in mol) ⟶ mass of *unknown* substance (in g)

Three additional pieces of data are needed to solve mass-mass problems: the molar mass of the *given* substance, the mole ratio, and the molar mass of the *unknown* substance.

SAMPLE PROBLEM 9-5

Tin(II) fluoride, SnF_2, is used in some toothpastes. It is made by the reaction of tin with hydrogen fluoride according to the following equation.

$$Sn(s) + 2HF(g) \longrightarrow SnF_2(s) + H_2(g)$$

How many grams of SnF_2 are produced from the reaction of 30.00 g of HF with Sn?

SOLUTION

1 ANALYZE

Given: amount of HF = 30.00 g
Unknown: mass of SnF_2 produced in grams

2 PLAN

The conversion factors needed are the molar masses of HF and SnF_2 and the mole ratio of SnF_2 to HF.

$$\text{g HF} \times \overset{\text{inverted molar mass}}{\frac{1 \text{ mol HF}}{\text{g HF}}} \times \overset{\text{mol ratio}}{\frac{\text{mol } SnF_2}{\text{mol HF}}} \times \overset{\text{molar mass}}{\frac{\text{g } SnF_2}{\text{mol } SnF_2}} = \text{g } SnF_2$$

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3 COMPUTE Use the periodic table to compute the molar masses of HF and SnF_2.

$$HF = 20.01 \text{ g/mol}$$
$$SnF_2 = 156.71 \text{ g/mol}$$

$$30.00 \text{ g HF} \times \frac{1 \text{ mol HF}}{20.01 \text{ g HF}} \times \frac{1 \text{ mol } SnF_2}{2 \text{ mol HF}} \times \frac{156.71 \text{ g } SnF_2}{1 \text{ mol } SnF_2} = 117.5 \text{ g } SnF_2$$

4 EVALUATE The answer is correctly rounded to four significant figures. The units cancel to leave g SnF_2, which matches the unknown. The answer is close to an estimated value of 120.

PRACTICE

1. Laughing gas (nitrous oxide, N_2O) is sometimes used as an anesthetic in dentistry. It is produced when ammonium nitrate is decomposed according to the following reaction.

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$$

   a. How many grams of NH_4NO_3 are required to produce 33.0 g of N_2O?

   b. How many grams of water are produced in this reaction?

Answer

1. a. 60.0 g NH_4NO_3

   b. 27.0 g H_2O

2. When copper metal is added to silver nitrate in solution, silver metal and copper(II) nitrate are produced. What mass of silver is produced from 100. g of Cu?

2. 339 g

3. What mass of aluminum is produced by the decomposition of 5.0 kg of Al_2O_3?

3. 2.6 kg

SECTION REVIEW

1. Balance the following equation. Then, based on the amount in moles of each reactant or product given, determine the corresponding amount in moles of each of the other reactants and products involved in the reaction.

$$NH_3 + O_2 \longrightarrow N_2 + H_2O$$

   a. 4 mol NH_3
   b. 4 mol N_2
   c. 4.5 mol O_2

2. One reaction that produces hydrogen gas can be represented by the following unbalanced chemical equation.

$$Mg(s) + HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

   a. What mass of HCl is consumed by the reaction of 2.50 mol of magnesium?
   b. What mass of each product is produced in part (a)?

3. Acetylene gas (C_2H_2) is produced as a result of the following reaction.

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

   a. If 32.0 g of CaC_2 are consumed in this reaction, how many moles of H_2O are needed?
   b. How many moles of each product would be formed?

4. When sodium chloride reacts with silver nitrate, silver chloride precipitates. What mass of AgCl is produced from 75.0 g of $AgNO_3$?

5. Acetylene gas, C_2H_2, used in welding, produces an extremely hot flame when it burns in pure oxygen according to the following reaction.

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$$

   How many grams of each product are produced when 2.50×10^4 g of C_2H_2 burns completely?

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SECTION 9-3

Limiting Reactants and Percent Yield

Objectives

- Describe a method for determining which of two reactants is a limiting reactant.
- Calculate the amount in moles or mass in grams of a product, given the amounts in moles or masses in grams of two reactants, one of which is in excess.
- Distinguish between theoretical yield, actual yield, and percent yield.
- Calculate percent yield, given the actual yield and quantity of a reactant.

In the laboratory, a reaction is rarely carried out with exactly the required amounts of each of the reactants. In most cases, one or more reactants is present in excess; that is, there is more than the exact amount required to react.

Once one of the reactants is used up, no more product can be formed. The substance that is completely used up first in a reaction is called the limiting reactant. *The* **limiting reactant** *is the reactant that limits the amounts of the other reactants that can combine and the amount of product that can form in a chemical reaction. The substance that is not used up completely in a reaction is sometimes called the* **excess reactant.** A limiting reactant may also be referred to as a limiting reagent.

The concept of the limiting reactant is analogous to the relationship between the number of people who want to take a certain airplane flight and the number of seats available in the airplane. If 400 people want to travel on the flight and only 350 seats are available, then only 350 people can go on the flight. The number of seats on the airplane limits the number of people who can travel. There are 50 people in excess.

The same reasoning can be applied to chemical reactions. Consider the reaction between carbon and oxygen to form carbon dioxide.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

According to the equation, one mole of carbon reacts with one mole of oxygen to form one mole of carbon dioxide. Suppose you could mix 5 mol of C with 10 mol of O_2 and allow the reaction to take place. Figure 9-5 shows that there is more oxygen than is needed to react with the carbon. Carbon is the limiting reactant in this situation, and it limits the amount of CO_2 that is formed. Oxygen is the excess reactant, and 5 mol of O_2 will be left over at the end of the reaction.

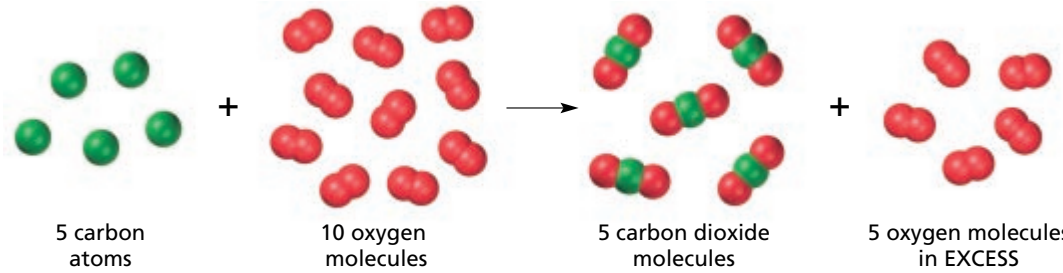

FIGURE 9-5 If you think of a mole as a multiple of molecules and atoms, you can see why the amount of O_2 is in excess.

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SAMPLE PROBLEM 9-6

Silicon dioxide (quartz) is usually quite unreactive but reacts readily with hydrogen fluoride according to the following equation.

$$SiO_2(s) + 4HF(g) \longrightarrow SiF_4(g) + 2H_2O(l)$$

If 2.0 mol of HF are exposed to 4.5 mol of SiO_2, which is the limiting reactant?

SOLUTION

1 ANALYZE

Given: amount of HF = 2.0 mol
amount of SiO_2 = 4.5 mol
Unknown: limiting reactant

2 PLAN

The given amount of either reactant is used to calculate the required amount of the other reactant. The calculated amount is then compared with the amount actually available, and the limiting reactant can be identified. We will choose to calculate the moles of SiO_2 required by the given amount of HF.

$$\text{mol HF} \times \frac{\text{mol } SiO_2}{\text{mol HF}} = \text{mol } SiO_2 \text{ required}$$

3 COMPUTE

$$2.0 \text{ mol HF} \times \frac{1 \text{ mol } SiO_2}{4 \text{ mol HF}} = 0.50 \text{ mol } SiO_2 \text{ required}$$

Under ideal conditions, the 2.0 mol of HF will require 0.50 mol of SiO_2 for complete reaction. Because the amount of SiO_2 available (4.5 mol) is more than the amount required (0.50 mol), the limiting reactant is HF.

4 EVALUATE

The calculated amount of SiO_2 is correctly given to two significant figures. Because each mole of SiO_2 requires 4 mol of HF, it is reasonable that HF is the limiting reactant because the molar amount of HF available is less than half that of SiO_2.

PRACTICE

1. Some rocket engines use a mixture of hydrazine, N_2H_4, and hydrogen peroxide, H_2O_2, as the propellant. The reaction is given by the following equation.

$$N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(g)$$

   a. Which is the limiting reactant in this reaction when 0.750 mol of N_2H_4 is mixed with 0.500 mol of H_2O_2?

   b. How much of the excess reactant, in moles, remains unchanged?

   c. How much of each product, in moles, is formed?

2. If 20.5 g of chlorine is reacted with 20.5 g of sodium, which reactant is in excess? How do you know?

Answer

1. a. H_2O_2

   b. 0.500 mol N_2H_4

   c. 0.250 mol N_2, 1.00 mol H_2O

2. Sodium is in excess because only 0.578 mol Na is needed.

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SAMPLE PROBLEM 9-7

The black oxide of iron, Fe_3O_4, occurs in nature as the mineral magnetite. This substance can also be made in the laboratory by the reaction between red-hot iron and steam according to the following equation.

$$3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$$

a. When 36.0 g of H_2O is mixed with 167 g of Fe, which is the limiting reactant?
b. What mass in grams of black iron oxide is produced?
c. What mass in grams of excess reactant remains when the reaction is completed?

SOLUTION

1 ANALYZE

Given: mass of H_2O = 36.0 g
mass of Fe = 167 g

Unknown: limiting reactant
mass of Fe_3O_4, in grams
mass of excess reactant remaining

2 PLAN

a. First convert both given masses in grams to amounts in moles. Choose one reactant and calculate the needed amount of the other to determine which is the limiting reactant. We have chosen Fe. The mole ratio from the balanced equation is 3 mol Fe for every 4 mol H_2O.

$$\text{g Fe} \times \overset{\text{inverted molar mass}}{\frac{1\text{ mol Fe}}{\text{g Fe}}} = \text{mol Fe available}$$

$$\text{g } H_2O \times \overset{\text{inverted molar mass}}{\frac{1\text{ mol } H_2O}{\text{g } H_2O}} = \text{mol } H_2O \text{ available}$$

$$\text{mol Fe} \times \overset{\text{mol ratio}}{\frac{\text{mol } H_2O}{\text{mol Fe}}} = \text{mol } H_2O \text{ required}$$

b. To find the maximum amount of Fe_3O_4 that can be produced, the given amount in moles of the limiting reactant must be used in a simple stoichiometric problem.

$$\text{limiting reactant (in mol)} \times \overset{\text{mol ratio}}{\frac{\text{mol } Fe_3O_4}{\text{mol limiting reactant}}} \times \overset{\text{molar mass}}{\frac{\text{g } Fe_3O_4}{\text{mol } Fe_3O_4}} = \text{g } Fe_3O_4 \text{ produced}$$

c. To find the amount of excess reactant remaining, the amount of the excess reactant that is consumed must first be determined. The given amount in moles of the limiting reactant must be used in a simple stoichiometric problem.

$$\text{limiting reactant (in mol)} \times \frac{\text{mol excess reactant}}{\text{mol limiting reactant}} \times \frac{\text{g excess reactant}}{\text{mol excess reactant}} = \text{g excess reactant consumed}$$

The amount of excess reactant remaining can then be found by subtracting the amount consumed from the amount originally present.

original g excess reactant – g excess reactant consumed = g excess reactant remaining

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3 COMPUTE

Use the periodic table to determine the molar masses of H_2O, Fe, and Fe_3O_4.

$H_2O = 18.02$ g/mol

Fe = 55.85 g/mol

$Fe_3O_4 = 231.55$ g/mol

$$36.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 2.00 \text{ mol } H_2O$$

$$167 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 2.99 \text{ mol Fe}$$

$$2.99 \text{ mol Fe} \times \frac{4 \text{ mol } H_2O}{3 \text{ mol Fe}} = 3.99 \text{ mol } H_2O \text{ required}$$

a. The required 3.99 mol of H_2O is more than the 2.00 mol of H_2O available, so H_2O is the limiting reactant.

b. $$2.00 \text{ mol } H_2O \times \frac{1 \text{ mol } Fe_3O_4}{4 \text{ mol } H_2O} \times \frac{231.55 \text{ g } Fe_3O_4}{\text{mol } Fe_3O_4} = 116 \text{ g } Fe_3O_4$$

c. $$2.00 \text{ mol } H_2O \times \frac{3 \text{ mol Fe}}{4 \text{ mol } H_2O} \times \frac{55.85 \text{ g Fe}}{\text{mol Fe}} = 83.8 \text{ g Fe consumed}$$

167 g Fe originally present − 83.8 g Fe consumed = 83.2 g Fe remaining

4 EVALUATE

Three significant digits are carried through each calculation. The result of the final subtraction is rounded to match the significance of the least accurately known number, that is, the units digit for the original mass of Fe. The mass of Fe_3O_4 is close to an estimated answer of 115, which is one-half of 230. The amount of the limiting reactant, H_2O, is about one-half the amount needed to use all of the Fe, so about one-half the Fe remains unreacted.

PRACTICE

1. Zinc and sulfur react to form zinc sulfide according to the following equation.

$$8Zn(s) + S_8(s) \longrightarrow 8ZnS(s)$$

   a. If 2.00 mol of Zn are heated with 1.00 mol of S_8, identify the limiting reactant.

   b. How many moles of excess reactant remain?

   c. How many moles of the product are formed?

2. Carbon reacts with steam, H_2O, at high temperatures to produce hydrogen and carbon monoxide.

   a. If 2.40 mol of carbon are exposed to 3.10 mol of steam, identify the limiting reactant.

   b. How many moles of each product are formed?

   c. What mass of each product is formed?

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Answer

1. a. Zn

   b. 0.75 mol S_8 remains

   c. 2.00 mol ZnS

2. a. carbon

   b. 2.40 mol H_2 and 2.40 mol CO

   c. 4.85 g H_2 and 67.2 g CO

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Quick LAB

Limiting Reactants in a Recipe

Wear oven mitts when handling heated items.

Materials

- 1/2 cup sugar
- 1/2 cup brown sugar
- 1 1/3 stick margarine (at room temperature)
- 1 egg
- 1/2 tsp. salt
- 1 tsp. vanilla
- 1/2 tsp. baking soda
- 1 1/2 cup flour
- 1 1/3 cup chocolate chips
- mixing bowl
- mixing spoon
- measuring spoons and cups
- cookie sheet
- oven preheated to 350°F

Procedure

1. In the mixing bowl, combine the sugars and margarine together until smooth. (An electric mixer will make this process go much faster.)
2. Add the egg, salt, and vanilla. Mix well.
3. Stir in the baking soda, flour, and chocolate chips. Chill the dough for an hour in the refrigerator for best results.
4. Divide the dough into 24 small balls about 3 cm in diameter. Place the balls on an ungreased cookie sheet.
5. Bake at 350°F for about 10 minutes, or until the cookies are light brown.

Yield: 24 cookies

Discussion

1. Suppose you are given the following amounts of ingredients:
   1 dozen eggs
   24 tsp. of vanilla
   1 lb. (82 tsp.) of salt
   1 lb. (84 tsp.) of baking soda
   3 cups of chocolate chips
   5 lb. (11 cups) of sugar
   2 lb. (4 cups) of brown sugar
   1 lb. (4 sticks) of margarine

   a. For each ingredient, calculate how many cookies could be prepared if all of that ingredient were consumed. (For example, the recipe shows that using 1 egg—with the right amounts of the other ingredients—yields 24 cookies. How many cookies can you make if the recipe is increased proportionately for 12 eggs?)

   b. To determine the limiting reactant for the new ingredients list, identify which ingredients will result in the fewest number of cookies.

   c. What is the maximum number of cookies that can be produced from the new amounts of ingredients?

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Percent Yield

The amounts of products calculated in the stoichiometric problems in this chapter so far represent theoretical yields. *The* **theoretical yield** *is the maximum amount of product that can be produced from a given amount of reactant.* In most chemical reactions, the amount of product obtained is less than the theoretical yield. There are many reasons for this. Some of the reactant may be used in competing side reactions that reduce the amount of the desired product. Also, once a product is formed, it often is usually collected in impure form, and some of the product is often lost during the purification process. *The measured amount of a product obtained from a reaction is called the* **actual yield** *of that product.*

Chemists are usually interested in the efficiency of a reaction. The efficiency is expressed by comparing the actual and theoretical yields. *The* **percent yield** *is the ratio of the actual yield to the theoretical yield, multiplied by 100.*

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

SAMPLE PROBLEM 9-8

Chlorobenzene, C_6H_5Cl, is used in the production of many important chemicals, such as aspirin, dyes, and disinfectants. One industrial method of preparing chlorobenzene is to react benzene, C_6H_6, with chlorine, as represented by the following equation.

$$C_6H_6(l) + Cl_2(g) \longrightarrow C_6H_5Cl(s) + HCl(g)$$

When 36.8 g of C_6H_6 react with an excess of Cl_2, the actual yield of C_6H_5Cl is 38.8 g. What is the percent yield of C_6H_5Cl?

SOLUTION

1 ANALYZE

Given: mass of C_6H_6 = 36.8 g
mass of Cl_2 = excess
actual yield of C_6H_5Cl = 38.8 g

Unknown: percent yield of C_6H_5Cl

2 PLAN

First do a mass-mass calculation to find the theoretical yield of C_6H_5Cl.

$$\text{g } C_6H_6 \times \frac{\overset{\text{inverted molar mass}}{\text{mol } C_6H_6}}{\text{g } C_6H_6} \times \frac{\overset{\text{mol ratio}}{\text{mol } C_6H_5Cl}}{\text{mol } C_6H_6} \times \frac{\overset{\text{molar mass}}{\text{g } C_6H_5Cl}}{\text{mol } C_6H_5Cl} = \text{g } C_6H_5Cl \text{ (theoretical yield)}$$

Then the percent yield can be found.

$$\text{percent yield } C_6H_5Cl = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

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3 COMPUTE Use the periodic table to determine the molar masses of C_6H_6 and C_6H_5Cl.

$$C_6H_6 = 78.12 \text{ g/mol}$$
$$C_6H_5Cl = 112.56 \text{ g/mol}$$

$$36.8 \text{ g } \cancel{C_6H_6} \times \frac{1 \text{ } \cancel{\text{mol } C_6H_6}}{78.12 \text{ } \cancel{\text{g } C_6H_6}} \times \frac{1 \text{ } \cancel{\text{mol } C_6H_5Cl}}{1 \text{ } \cancel{\text{mol } C_6H_6}} \times \frac{112.56 \text{ g } C_6H_5Cl}{\cancel{\text{mol } C_6H_5Cl}} = 53.0 \text{ g } C_6H_5Cl \text{ (theoretical yield)}$$

$$\text{percent yield} = \frac{38.8 \text{ g}}{53.0 \text{ g}} \times 100 = 73.2\%$$

4 EVALUATE The answer is correctly rounded to three significant figures to match those in 36.8 g C_6H_6. The units have canceled correctly. The theoretical yield is close to an estimated value of 50 g, (one-half of 100 g). The percent yield is close to an estimated value of 80%, (40/50 × 100).

PRACTICE

1. Methanol can be produced through the reaction of CO and H_2 in the presence of a catalyst. *Answer* 79.8%

$$CO(g) + 2H_2(g) \xrightarrow{\text{catalyst}} CH_3OH(l)$$

If 75.0 g of CO reacts to produce 68.4 g CH_3OH, what is the percent yield of CH_3OH?

2. Aluminum reacts with excess copper(II) sulfate according to the reaction given below. If 1.85 g of Al react and the percent yield of Cu is 56.6%, what mass of Cu is produced? *Answer* 3.70 g

$$Al(s) + CuSO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + Cu(s) \text{ (unbalanced)}$$

SECTION REVIEW

1. Carbon disulfide burns in oxygen to yield carbon dioxide and sulfur dioxide according to the following chemical equation.

$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$$

   a. If 1.00 mol of CS_2 is combined with 1.00 mol of O_2, identify the limiting reactant.
   b. How many moles of excess reactant remain?
   c. How many moles of each product are formed?

2. Metallic magnesium reacts with steam to produce magnesium hydroxide and hydrogen gas.
   a. If 16.2 g of Mg are heated with 12.0 g of H_2O, what is the limiting reactant?
   b. How many moles of the excess reactant are left?
   c. How many grams of each product are formed?

3. a. What is the limiting reactant when 19.9 g of CuO are exposed to 2.02 g of H_2 according to the following equation?

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$$

   b. How many grams of Cu are produced?

4. Quicklime, CaO, can be prepared by roasting limestone, $CaCO_3$, according to the following reaction.

$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$.

When 2.00×10^3 g of $CaCO_3$ are heated, the actual yield of CaO is 1.05×10^3 g. What is the percent yield?

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CHAPTER 9 REVIEW

CHAPTER SUMMARY

9-1

- Reaction stoichiometry involves the mass relationships between reactants and products in a chemical reaction.
- A *mole ratio* is the conversion factor that relates the amount in moles of any two substances in a chemical reaction. The mole ratio is derived from the balanced equation.
- Amount of a substance is expressed in moles, and mass of a substance is expressed using mass units such as grams, kilograms, and milligrams.
- Mass and amount of substance are quantities, whereas moles and grams are units.
- A balanced chemical equation is necessary to solve any stoichiometric problem.

Vocabulary

composition stoichiometry (275) mole ratio (276) reaction stoichiometry (275)

9-2

- In an ideal stoichiometric calculation, the mass or the amount of any reactant or product can be calculated if the balanced chemical equation and the mass or amount of any other reactant or product are known.

9-3

- In actual reactions, the reactants are usually combined in proportions different from the precise proportions required for complete reaction.
- The limiting reactant controls the maximum possible amount of product formed.
- Given certain quantities of reactants, the quantity of the product is always less than the maximum possible. Percent yield shows the relationship between the theoretical yield and actual yield for the product of a reaction.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

Vocabulary

actual yield (293) limiting reactant (288) percent yield (293) theoretical yield (293)
excess reactant (288)

REVIEWING CONCEPTS

1. a. Explain the concept of *mole ratio* as used in reaction-stoichiometry problems.
b. What is the source of this value? (9-1)

2. For each of the following chemical equations, write all possible mole ratios:
a. $2Ca + O_2 \longrightarrow 2CaO$
b. $Mg + 2HF \longrightarrow MgF_2 + H_2$ (9-1)

3. a. What is molar mass?
b. What is its role in reaction stoichiometry? (9-2)

4. Distinguish between ideal and real stoichiometric calculations. (9-3)

5. Distinguish between the limiting reactant and the excess reactant in a chemical reaction. (9-3)

6. a. Distinguish between the theoretical and actual yields in stoichiometric calculations.
b. How do the values of the theoretical and actual yields generally compare? (9-3)

7. What is the percent yield of a reaction? (9-3)

8. Why are actual yields generally less than those calculated theoretically? (9-3)

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PROBLEMS

General Stoichiometry

Do not assume that equations without listed coefficients are balanced.

9. Given the chemical equation $Na_2CO_3(aq) + Ca(OH)_2(s) \longrightarrow 2NaOH(aq) + CaCO_3(s)$, determine to two decimal places the molar masses of all substances involved, and then write them as conversion factors.

10. Hydrogen and oxygen react under a specific set of conditions to produce water according to the following: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$.
a. How many moles of hydrogen would be required to produce 5.0 mol of water?
b. How many moles of oxygen would be required? (Hint: See Sample Problem 9-1.)

11. a. If 4.50 mol of ethane, C_2H_6, undergo combustion according to the unbalanced equation $C_2H_6 + O_2 \longrightarrow CO_2 + H_2O$, how many moles of oxygen are required?
b. How many moles of each product are formed?

12. Sodium chloride is produced from its elements through a synthesis reaction. What mass of each reactant would be required to produce 25.0 mol of sodium chloride?

13. Iron is generally produced from iron ore through the following reaction in a blast furnace: $Fe_2O_3(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$.
a. If 4.00 kg of Fe_2O_3 are available to react, how many moles of CO are needed?
b. How many moles of each product are formed?

14. Methanol, CH_3OH, is an important industrial compound that is produced from the following reaction: $CO(g) + H_2(g) \longrightarrow CH_3OH(g)$. What mass of each reactant would be needed to produce 100.0 kg of methanol? (Hint: See Sample Problem 9-5.)

15. Nitrogen combines with oxygen in the atmosphere during lightning flashes to form nitrogen monoxide, NO, which then reacts further with O_2 to produce nitrogen dioxide, NO_2.
a. What mass of NO_2 is formed when NO reacts with 384 g of O_2?
b. How many grams of NO are required to react with this amount of O_2?

16. As early as 1938, the use of NaOH was suggested as a means of removing CO_2 from the cabin of a spacecraft according to the following reaction: $NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$.
a. If the average human body discharges 925.0 g of CO_2 per day, how many moles of NaOH are needed each day for each person in the spacecraft?
b. How many moles of each product are formed?

17. The double-replacement reaction between silver nitrate and sodium bromide produces silver bromide, a component of photographic film.
a. If 4.50 mol of silver nitrate reacts, what mass of sodium bromide is required?
b. What mass of silver bromide is formed?

18. In a soda-acid fire extinguisher, concentrated sulfuric acid reacts with sodium hydrogen carbonate to produce carbon dioxide, sodium sulfate, and water.
a. How many moles of sodium hydrogen carbonate would be needed to react with 150.0 g of sulfuric acid?
b. How many moles of each product would be formed?

19. Sulfuric acid reacts with sodium hydroxide according to the following:

$$H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O.$$

a. Balance the equation for this reaction.
b. What mass of H_2SO_4 would be required to react with 0.75 mol of NaOH?
c. What mass of each product is formed by this reaction? (Hint: See Sample Problem 9-2.)

20. Copper reacts with silver nitrate through single replacement.
a. If 2.25 g of silver are produced from the reaction, how many moles of copper(II) nitrate are also produced?
b. How many moles of each reactant are required in this reaction? (Hint: See Sample Problem 9-4.)

21. Aspirin, $C_9H_8O_4$, is produced through the following reaction of salicylic acid, $C_7H_6O_3$, and acetic anhydride, $C_4H_6O_3$: $C_7H_6O_3(s) + C_4H_6O_3(l) \longrightarrow C_9H_8O_4(s) + HC_2H_3O_2(l)$.
a. What mass of aspirin (in kg) could be produced from 75.0 mol of salicylic acid?

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b. What mass of acetic anhydride (in kg) would be required?
c. At 20°C, how many liters of acetic acid, $HC_2H_3O_2$, would be formed? The density of $HC_2H_3O_2$ is 1.05 g/cm^3.

Limiting Reactant

22. Given the reactant amounts specified in each chemical equation, determine the limiting reactant in each case:

a. $\underset{2.0\ mol}{HCl} + \underset{2.5\ mol}{NaOH} \longrightarrow NaCl + H_2O$

b. $\underset{2.5\ mol}{Zn} + \underset{6.0\ mol}{2HCl} \longrightarrow ZnCl_2 + H_2$

c. $\underset{4.0\ mol}{2Fe(OH)_3} + \underset{6.5\ mol}{3H_2SO_4} \longrightarrow Fe_2(SO_4)_3 + 6H_2O$

(Hint: See Sample Problem 9-6.)

23. For each reaction specified in Problem 22, determine the amount in moles of excess reactant that remains. (Hint: See Sample Problem 9-7.)

24. For each reaction specified in Problem 22, calculate the amount in moles of each product formed.

25. a. If 2.50 mol of copper and 5.50 mol of silver nitrate are available to react by single replacement, identify the limiting reactant.
b. Determine the amount in moles of excess reactant remaining.
c. Determine the amount in moles of each product formed.
d. Determine the mass of each product formed.

26. Sulfuric acid reacts with aluminum hydroxide by double replacement.
a. If 30.0 g of sulfuric acid react with 25.0 g of aluminum hydroxide, identify the limiting reactant.
b. Determine the mass of excess reactant remaining.
c. Determine the mass of each product formed. Assume 100% yield.

27. The energy used to power one of the Apollo lunar missions was supplied by the following overall reaction: $2N_2H_4 + (CH_3)_2N_2H_2 + 3N_2O_4 \longrightarrow 6N_2 + 2CO_2 + 8H_2O$. For the phase of the mission when the lunar module ascended from the surface of the moon, a total of 1200. kg of N_2H_4 were available to react with 1000. kg of $(CH_3)_2N_2H_2$ and 4500. kg of N_2O_4.
a. For this portion of the flight, which of the allocated components was used up first?
b. How much water, in kilograms, was put into the lunar atmosphere through this reaction?

Percent Yield

28. Calculate the indicated quantity for each of the various chemical reactions given:
a. theoretical yield = 20.0 g, actual yield = 15.0 g, percent yield = ?
b. theoretical yield = 1.0 g, percent yield = 90.0%, actual yield = ?
c. theoretical yield = 5.00 g, actual yield = 4.75 g, percent yield = ?
d. theoretical yield = 3.45 g, percent yield = 48.0%, actual yield = ?

29. The percentage yield for the reaction

$PCl_3 + Cl_2 \longrightarrow PCl_5$

is 83.2%. What mass of PCl_5 is expected from the reaction of 73.7 g of PCl_3 with excess chlorine?

30. The Ostwald Process for producing nitric acid from ammonia consists of the following steps:

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$
$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
$3NO_2(g) + H_2O(g) \longrightarrow 2HNO_3(aq) + NO(g)$

If the yield in each step is 94.0%, how many grams of nitric acid can be produced from 5.00 kg of ammonia?

MIXED REVIEW

31. Magnesium is obtained from sea water. $Ca(OH)_2$ is added to sea water to precipitate $Mg(OH)_2$. The precipitate is filtered and reacted with HCl to produce $MgCl_2$. The $MgCl_2$ is electrolyzed to produce Mg and Cl_2. If 185.0 g of magnesium are recovered from 1000. g of $MgCl_2$, what is the percent yield for this reaction?

32. Phosphate baking powder is a mixture of starch, sodium hydrogen carbonate, and calcium dihydrogen phosphate. When mixed with water, phosphate baking powder releases carbon dioxide gas, causing a dough or batter to bubble and rise.

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$2NaHCO_3(aq) + Ca(H_2PO_4)_2(aq) \longrightarrow Na_2HPO_4(aq) + CaHPO_4(aq) + 2CO_2(g) + 2H_2O(l)$

If 0.750 L of CO_2 is needed for a cake and each kilogram of baking powder contains 168 g of $NaHCO_3$, how many grams of baking powder must be used to generate this amount of CO_2? The density of CO_2 at baking temperature is about 1.20 g/L.

33. Coal gasification is a process that converts coal into methane gas. If this reaction has a percent yield of 85.0%, what mass of methane can be obtained from 1250 g of carbon?

$$2C(s) + 2H_2O(l) \longrightarrow CH_4(g) + CO_2(g)$$

34. If the percent yield for the coal gasification process is increased to 95%, what mass of methane can be obtained from 2750 g of carbon?

35. Builders and dentists must store plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O$, in airtight containers to prevent it from absorbing water vapor from the air and changing to gypsum, $CaSO_4 \cdot 2H_2O$. How many liters of water evolve when 5.00 L of gypsum are heated at 110°C to produce plaster of Paris? At 110°C, the density of $CaSO_4 \cdot 2H_2O$ is 2.32 g/mL, and the density of water vapor is 0.581 g/mL.

36. Gold can be recovered from sea water by reacting the water with zinc, which is refined from zinc oxide. The zinc displaces the gold in the water. What mass of gold can be recovered if 2.00 g of ZnO and an excess of sea water are available?

$$2ZnO(s) + C(s) \longrightarrow 2Zn(s) + CO_2(g)$$
$$2Au^{3+}(aq) + 3Zn(s) \longrightarrow 3Zn^{2+}(aq) + 2Au(s)$$

CRITICAL THINKING

37. Relating Ideas The chemical equation is a good source of information concerning a reaction. Explain the relationship that exists between the actual yield of a reaction product and the chemical equation of the product.

38. Analyzing Results Very seldom are chemists able to achieve a 100% yield of a product from a chemical reaction. However, the yield of a reaction is usually important because of the expense involved in producing less product. For example, when magnesium metal is heated in a crucible at high temperatures, the product magnesium oxide, MgO, is formed. Based on your analysis of the reaction, describe some of the actions you would take to increase your percent yield. The reaction is as follows:

$$2\ Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

39. Analyzing Results In the lab, you run an experiment that appears to have a percent yield of 115%. Propose reasons for this result. Can an actual yield ever exceed a theoretical yield? Explain your answer.

40. Relating Ideas Explain the stoichiometry of blowing air on a smoldering campfire to keep the coals burning.

TECHNOLOGY & LEARNING

41. Graphing Calculator Calculating Percent Yield of a Chemical Reaction

The graphing calculator can run a program that calculates the percent yield of a chemical reaction when you enter the actual yield and the theoretical yield. Using an example in which the actual yield is 38.8 g and the theoretical yield is 53.2 g, you will calculate the percent yield. First, the program will carry out the calculation. Then it will be used to make other calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

Note: all answers are written with three significant figures.

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a. What is the percent yield when the actual yield is 27.3 g and the theoretical yield is 44.6 g?
b. What is the percent yield when the actual yield is 5.4 g and the theoretical yield is 9.2 g?
c. What actual yield/theoretical yield pair produced the largest percent yield?

HANDBOOK SEARCH

42. The steel-making process described in the Transition Metal section of the *Elements Handbook* shows the equation for the formation of iron carbide. Use this equation to answer the following.
a. If 3.65×10^3 kg of iron is used in a steelmaking process, what is the minimum mass of carbon needed to react with all of the iron?
b. What is the theoretical mass of iron carbide formed?

43. The reaction of aluminum with oxygen to produce a protective coating for the metal's surface is described in the discussion of aluminum in Group 13 of the *Elements Handbook*. Use this equation to answer the following.
a. What mass of aluminum oxide would theoretically be formed if a 30.0 g piece of aluminum foil reacted with excess oxygen?
b. Why would you expect the actual yield from this reaction to be far less than the mass you calculated in item (a)?

44. The reactions of oxide compounds to produce carbonates, phosphates, and sulfates are described in the section on oxides in Group 16 of the *Elements Handbook*. Use those equations to answer the following.
a. What mass of CO_2 is needed to react with 154.6 g of MgO?
b. What mass of magnesium carbonate is produced?
c. 45.7 g of P_4O_{10} is reacted with an excess of calcium oxide. What mass of calcium phosphate is produced?

RESEARCH & WRITING

45. Research the history of the Haber process for the production of ammonia. What was the significance of this process in history? How is this process related to the discussion of reaction yields in this chapter?

ALTERNATIVE ASSESSMENT

46. Performance Just as reactants combine in certain proportions to form a product, colors can be combined to create other colors. Artists do this all the time to find just the right color for their paintings. Using poster paint, determine the proportions of primary pigments used to create the following colors. Your proportions should be such that anyone could mix the color perfectly. (Hint: Don't forget to record the amount of the primary pigment and water used when you mix them.)

47. Performance Write two of your own sample problems that are descriptions of how to solve a mass-mass problem. Assume that your sample problems will be used by other students to learn how to solve mass-mass problems.

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CHAPTER 10

Physical Characteristics of Gases

The density of a gas decreases as its temperature increases.

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The Kinetic-Molecular Theory of Matter

SECTION 10-1

Objectives

- State the kinetic-molecular theory of matter, and describe how it explains certain properties of matter.
- List the five assumptions of the kinetic-molecular theory of gases. Define the terms *ideal gas* and *real gas*.
- Describe each of the following characteristic properties of gases: expansion, density, fluidity, compressibility, diffusion, and effusion.
- Describe the conditions under which a real gas deviates from "ideal" behavior.

In Chapter 1, you read that matter exists on Earth in the forms of solids, liquids, and gases. Although it is not usually possible to observe individual particles directly, scientists have studied large groups of these particles as they occur in solids, liquids, and gases.

In the late nineteenth century, scientists developed the kinetic-molecular theory of matter to account for the behavior of the atoms and molecules that make up matter. *The* **kinetic-molecular theory** *is based on the idea that particles of matter are always in motion.* The theory can be used to explain the properties of solids, liquids, and gases in terms of the energy of particles and the forces that act between them. In this section, you will study the theory as it applies to gas molecules. In that form, it is called the kinetic-molecular theory of gases.

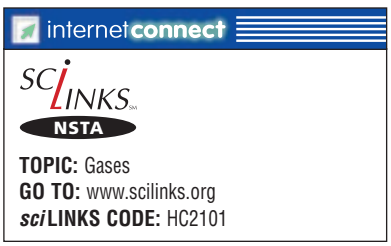
The Kinetic-Molecular Theory of Gases

The kinetic-molecular theory can help you understand the behavior of gas molecules and the physical properties of gases. The theory provides a model of what is called an ideal gas. *An* **ideal gas** *is an imaginary gas that perfectly fits all the assumptions of the kinetic-molecular theory.*

The kinetic-molecular theory of gases is based on the following five assumptions:

1. *Gases consist of large numbers of tiny particles that are far apart relative to their size.* These particles, usually molecules or atoms, typically occupy a volume about 1000 times greater than the volume occupied by particles in the liquid or solid state. Thus, molecules of gases are much farther apart than those of liquids or solids. Most of the volume occupied by a gas is empty space. This accounts for the lower density of gases compared with that of liquids and solids. It also explains the fact that gases are easily compressed.
2. *Collisions between gas particles and between particles and container walls are elastic collisions. An* **elastic collision** *is one in which there is no net loss of kinetic energy.* Kinetic energy is transferred between two particles during collisions. However, the total kinetic energy of the two particles remains the same as long as temperature is constant.

Module 1: States of Matter/Classes of Matter



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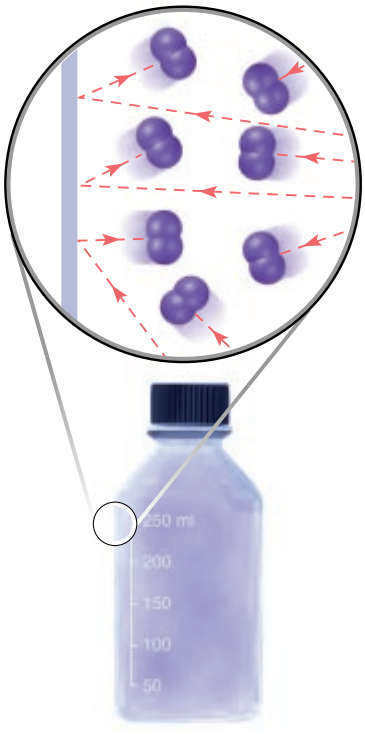

FIGURE 10-1 Gas particles travel in a straight-line motion until they collide with each other or the walls of their container.

3. *Gas particles are in continuous, rapid, random motion. They therefore possess kinetic energy, which is energy of motion.* Gas particles move in all directions, as shown in Figure 10-1. The kinetic energy of the particles overcomes the attractive forces between them, except near the temperature at which the gas condenses and becomes a liquid.
4. *There are no forces of attraction or repulsion between gas particles.* You can think of ideal gas molecules as behaving like small billiard balls. When they collide, they do not stick together but immediately bounce apart.
5. *The average kinetic energy of gas particles depends on the temperature of the gas.* The kinetic energy of any moving object, including a particle, is given by the following equation.

$$KE = \frac{1}{2}mv^2$$

In the equation, m is the mass of the particle and v is its speed. Because all the particles of a specific gas have the same mass, their kinetic energies depend only on their speeds. The average speeds and kinetic energies of gas particles increase with an increase in temperature and decrease with a decrease in temperature.

All gases at the same temperature have the same average kinetic energy. Therefore, at the same temperature, lighter gas particles, such as hydrogen molecules, have higher average speeds than do heavier gas particles, such as oxygen molecules.

The Kinetic-Molecular Theory and the Nature of Gases

The kinetic-molecular theory applies only to ideal gases. Although ideal gases do not actually exist, many gases behave nearly ideally if pressure is not very high or temperature is not very low. In the following sections, you will see how the kinetic-molecular theory accounts for the physical properties of gases.

Expansion

Gases do not have a definite shape or a definite volume. They completely fill any container in which they are enclosed, and they take its shape. A gas transferred from a one-liter vessel to a two-liter vessel will quickly expand to fill the entire two-liter volume. The kinetic-molecular theory explains these facts. According to the theory, gas particles move rapidly in all directions (assumption 3) without significant attraction or repulsion between them (assumption 4).

Fluidity

Because the attractive forces between gas particles are insignificant (assumption 4), gas particles glide easily past one another. This ability to

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flow causes gases to behave similarly to liquids. *Because liquids and gases flow, they are both referred to as* **fluids.**

Low Density

The density of a substance in the gaseous state is about 1/1000 the density of the same substance in the liquid or solid state. That is because the particles are so much farther apart in the gaseous state (assumption 1).

Compressibility

During compression, the gas particles, which are initially very far apart (assumption 1), are crowded closer together. The volume of a given sample of a gas can be greatly decreased. Steel cylinders containing gases under pressure are widely used in industry. When they are full, such cylinders may contain 100 times as many particles of gas as would be contained in nonpressurized containers of the same size.

Diffusion and Effusion

Gases spread out and mix with one another, even without being stirred. If the stopper is removed from a container of ammonia in a room, ammonia gas will mix uniformly with the air and spread throughout the room. The random and continuous motion of the ammonia molecules (assumption 3) carries them throughout the available space. *Such spontaneous mixing of the particles of two substances caused by their random motion is called* **diffusion.**

The rate of diffusion of one gas through another depends on three properties of the gas particles: their speeds, their diameters, and the attractive forces between them. In Figure 10-2, hydrogen gas diffuses rapidly into other gases at the same temperature because its molecules are lighter and move faster than the molecules of the other gases.

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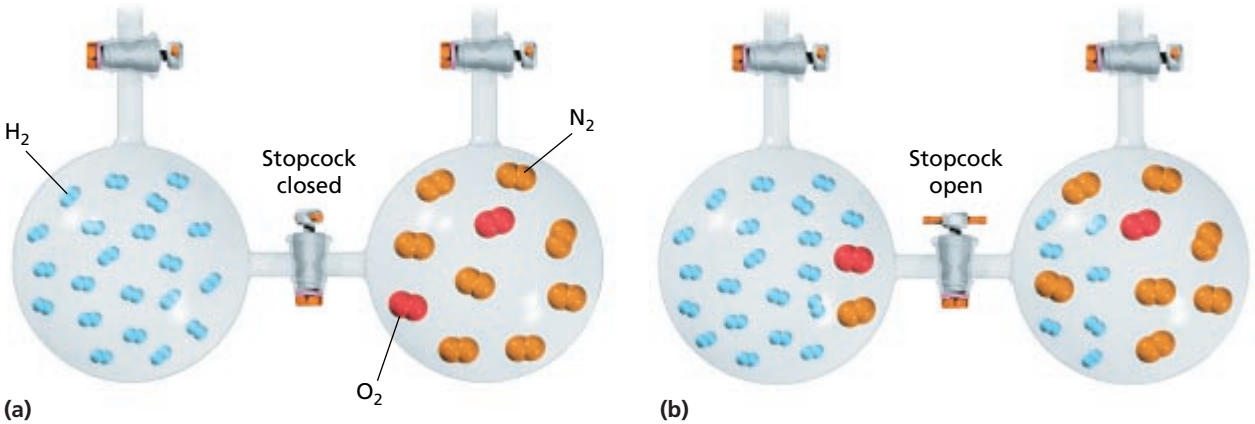

FIGURE 10-2 When hydrogen gas in a flask is allowed to mix with air at the same pressure in another flask, the low-mass molecules of hydrogen diffuse rapidly into the flask with the air. The heavier molecules of nitrogen and oxygen in the air diffuse more slowly into the flask with the hydrogen.

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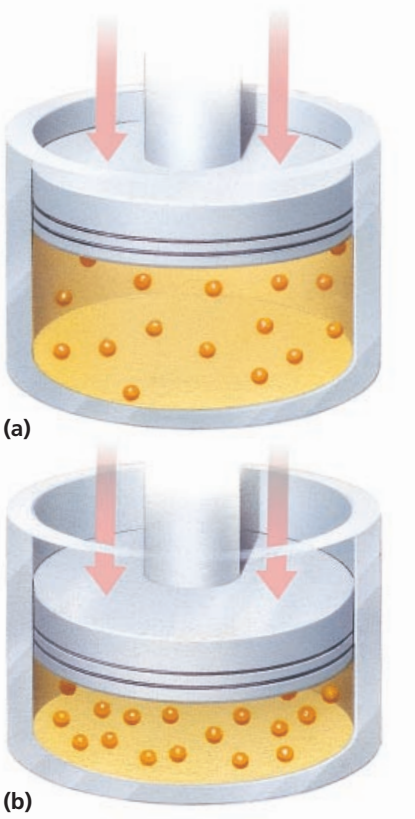

FIGURE 10-3 (a) Gas molecules in a car engine cylinder expand to fill the cylinder. (b) As pressure is exerted on them, the gas molecules move closer together, reducing their volume.

Diffusion is a process by which particles of a gas spread out spontaneously and mix with other gases. In contrast, **effusion** *is a process by which gas particles pass through a tiny opening*. The rates of effusion of different gases are directly proportional to the velocities of their particles. Because of this proportionality, molecules of low mass effuse faster than molecules of high mass.

Deviations of Real Gases from Ideal Behavior

When their particles are far enough apart and have enough kinetic energy, most gases behave ideally. However, all real gases deviate to some degree from ideal-gas behavior. *A* **real gas** *is a gas that does not behave completely according to the assumptions of the kinetic-molecular theory*. In 1873, Johannes van der Waals accounted for this deviation from ideal behavior by pointing out that particles of real gases occupy space and exert attractive forces on each other. At very high pressures and low temperatures, the deviation may be considerable. Under such conditions, the particles will be closer together and their kinetic energy will be insufficient to completely overcome the attractive forces. These conditions are illustrated in Figure 10-3.

The kinetic-molecular theory is more likely to hold true for gases whose particles have little attraction for each other. The noble gases, such as helium, He, and neon, Ne, show essentially ideal gas behavior over a wide range of temperatures and pressures. The particles of these gases are monatomic and thus nonpolar. The particles of gases, such as nitrogen, N_2, and hydrogen, H_2, are nonpolar diatomic molecules. The behavior of these gases most closely approximates that of the ideal gas under certain conditions. The more polar a gas's molecules are, the greater the attractive forces between them and the more the gas will deviate from ideal gas behavior. For example, highly polar gases, such as ammonia, NH_3, and water vapor, deviate from ideal behavior to a larger degree than nonpolar gases.

SECTION REVIEW

1. Use the kinetic-molecular theory to explain each of the following properties of gases: expansion, fluidity, low density, compressibility, and diffusion.
2. Describe the conditions under which a real gas is most likely to behave ideally.
3. State the two factors that van der Waals proposed to explain why real gases deviate from ideal behavior.
4. Which of the following gases would you expect to deviate significantly from ideal behavior: He, O_2, H_2, H_2O, N_2, HCl, or NH_3?

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Carbon Monoxide Catalyst—Stopping the Silent Killer

Colorless, odorless, and deadly—carbon monoxide, "the silent killer," causes the deaths of hundreds of Americans every year. When fuel does not burn completely in a combustion process, carbon monoxide is produced. Often this occurs in a malfunctioning heater, furnace, or fireplace. When the carbon monoxide is inhaled, it bonds to the hemoglobin in the blood, leaving the body oxygen starved. Before people realize a combustion device is malfunctioning, it's often too late.

$$O_2Hb + CO \longrightarrow COHb + O_2$$

Carbon monoxide, CO, has almost 200 times the affinity to bind with the hemoglobin, Hb, in the blood as oxygen. This means if the body has a choice, it will bind to carbon monoxide over oxygen. If enough carbon monoxide is present in the blood, it can be fatal.

Carbon monoxide poisoning can be prevented by installing filters that absorb the gas. After a time, however, filters become saturated, and then carbon monoxide can pass freely into the air. The best way to prevent carbon monoxide poisoning is not just to filter out the gas, but to eliminate it completely.

The solution came to research chemists at NASA who were working on a problem with a space-based laser. In order to operate properly, NASA's space-based carbon dioxide laser needed to be fed a continuous supply of CO_2. This was necessary because as a byproduct of its operation, the laser degraded some of the CO_2 into carbon monoxide and oxygen. To address this problem, NASA scientists developed a catalyst made of tin oxide and platinum that oxidized the waste carbon monoxide back into carbon dioxide. The NASA scientists then realized that this catalyst had the potential to be used in many applications here on Earth, including removing carbon monoxide from houses and other buildings.

Typically, a malfunctioning heater circulates the carbon monoxide it produces through its air intake system back into a dwelling space. By installing the catalyst in the air intake, any carbon monoxide would be oxidized to non-toxic carbon dioxide before it reentered the room.

"The form of our catalyst is a very thin coating on some sort of a support, or substrate as we call it," says NASA chemist David Schryer. "And that support, or substrate, can be any one of a number of things. The great thing about a catalyst is that the only thing that matters about it is its surface. So a catalyst can be incredibly thin and still be very effective."

The idea of using catalysts to oxidize gases is not a new one. Catalytic converters in cars oxidize carbon monoxide and unburned hydrocarbons to minimize pollution. Many substances are oxidized into new materials for manufacturing purposes. But both of these types of catalytic reactions occur at very high temperatures. NASA's catalyst is special, because it's able to eliminate carbon monoxide at room temperature.

According to David Schryer, low-temperature catalysts constitute a whole new class of catalysts with abundant applications for the future.

How did NASA's research on the space-based carbon dioxide laser result in a benefit for consumers?

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SECTION 10-2

Pressure

Objectives

- Define *pressure* and relate it to force.
- Describe how pressure is measured.
- Convert units of pressure.
- State the standard conditions of temperature and pressure.

Suppose you have a one-liter bottle of air. How much air do you actually have? The expression *a liter of air* means little unless the conditions at which the volume is measured are known. A liter of air can be compressed to a few milliliters. It can also be allowed to expand to fill an auditorium.

To describe a gas fully, you need to state four measurable quantities: volume, temperature, number of molecules, and pressure. You already know what is meant by volume, temperature, and number of molecules. In this section, you will learn about pressure and its measurement. Then, in Section 10-3, you will examine the mathematical relationships between volume, temperature, number of gas molecules, and pressure.

Pressure and Force

If you blow air into a rubber balloon, the balloon will increase in size. The volume increase is caused by the collisions of molecules of air with the inside walls of the balloon. The collisions cause an outward push, or force, against the inside walls. **Pressure** *(P) is defined as the force per unit area on a surface*. The equation defining pressure follows.

FIGURE 10-4 The pressure the ballet dancer exerts against the floor depends on the area of contact. The smaller the area of contact, the greater the pressure.

(a) Area of contact = 325 cm²

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{500\ \text{N}}{325\ \text{cm}^2} = 1.5\ \text{N/cm}^2$$

(b) Area of contact = 13 cm²

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{500\ \text{N}}{13\ \text{cm}^2} = 38.5\ \text{N/cm}^2$$

(c) Area of contact = 6.5 cm²

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{500\ \text{N}}{6.5\ \text{cm}^2} = 77\ \text{N/cm}^2$$

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$$pressure = \frac{force}{area}$$

The SI unit for force is the **newton,** abbreviated N. *It is the force that will increase the speed of a one kilogram mass by one meter per second each second it is applied.* At Earth's surface, each kilogram of mass exerts 9.8 N of force, due to gravity. Consider a ballet dancer with a mass of 51 kg, as shown in Figure 10-4. A mass of 51 kg exerts a force of 500 N (51 × 9.8) on Earth's surface. No matter how the dancer stands, she exerts that much force against the floor. However, the pressure she exerts against the floor depends on the area of contact. When she rests her weight on the soles of both feet, as shown in Figure 10-4(a), the area of contact with the floor is about 325 cm^2. The pressure, or force per unit area, when she stands in this manner is 500 N/325 cm^2. That equals roughly 1.5 N/cm^2. When she stands on her toes, as in Figure 10-4(b), the total area of contact with the floor is only 13 cm^2. The pressure exerted is then equal to 500 N/13 cm^2—roughly 38.5 N/cm^2. And when she stands on one toe, as in Figure 10-4(c), the pressure she exerts is twice that, or about 77 N/cm^2. Thus, the same force applied to a smaller area results in a greater pressure.

Gas molecules exert pressure on any surface with which they collide. The pressure exerted by a gas depends on volume, temperature, and the number of molecules present.

The atmosphere—the blanket of air surrounding Earth—exerts pressure. Figure 10-5 shows that atmospheric pressure at sea level is about equal to the weight of a 1.03 kg mass per square centimeter of surface, or 10.1 N/cm^2. The pressure of the atmosphere can be thought of as caused by the weight of the gases that compose the atmosphere. The atmosphere contains about 78% nitrogen, 21% oxygen, and 1% other gases, including

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Module 6: Gas Laws

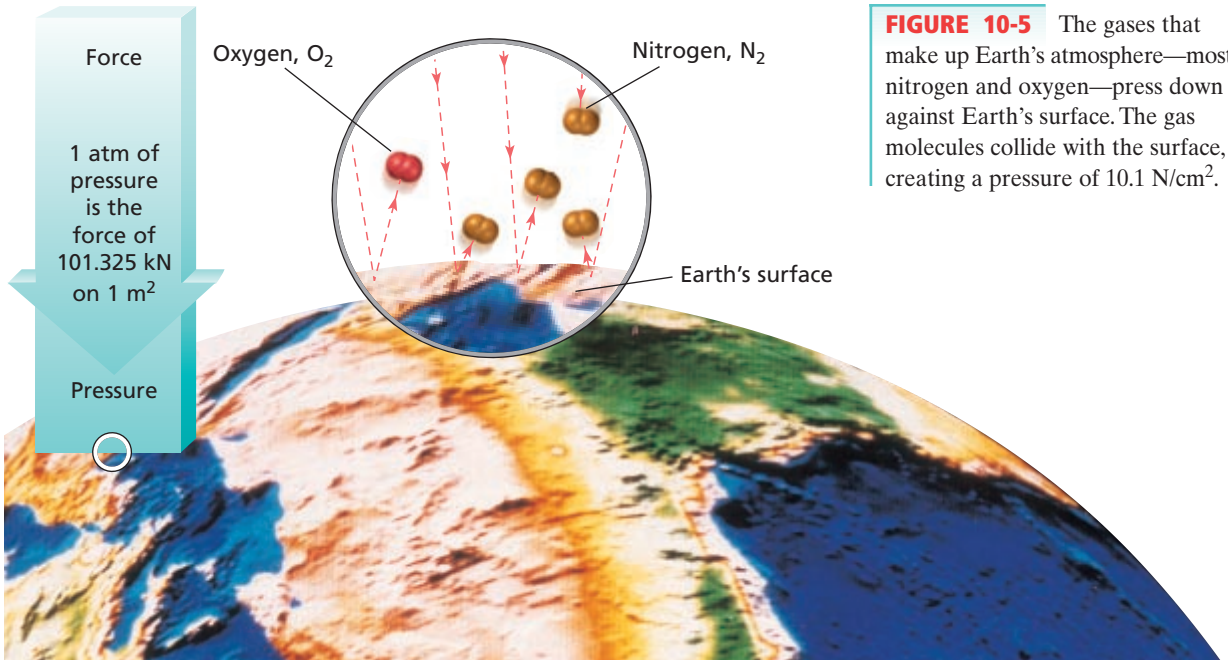

FIGURE 10-5 The gases that make up Earth's atmosphere—mostly nitrogen and oxygen—press down against Earth's surface. The gas molecules collide with the surface, creating a pressure of 10.1 N/cm^2.

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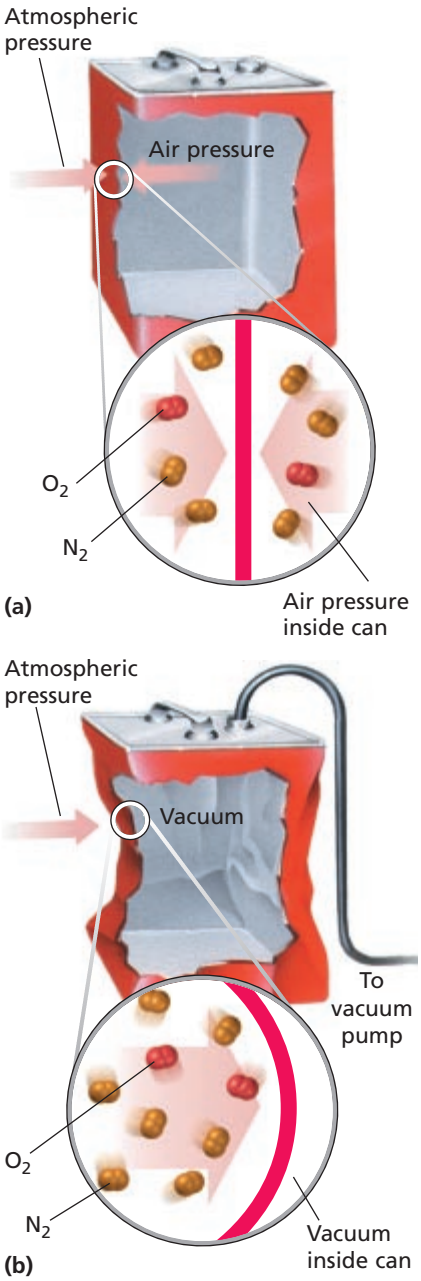

FIGURE 10-6 (a) The "empty" can has the mixture of gases in air inside that push outward and balance the atmospheric pressure that pushes inward. (b) When the air inside the can is removed by a vacuum pump, there is insufficient force to balance the atmospheric pressure. As a result, the can collapses.

argon and carbon dioxide. Atmospheric pressure is the sum of the individual pressures of the various gases in the atmosphere.

To understand the concept of gas pressure and its magnitude, consider the model of an "empty" can shown in Figure 10-6(a). The can does contain a small amount of air. The atmosphere exerts a pressure of 10.1 N/cm^2 against the outside of the can. If the can measures 15 cm × 10 cm × 28 cm, it has a total area of 1700 cm^2. The resulting inward force on the can is greater than 1.0 metric ton of weight. The air inside the can pushes outward and balances the atmosphere's inward-pushing force. If a vacuum pump is used to remove the air from the can, as shown in Figure 10-6(b), the balancing outward force is removed. As a result, the unbalanced force due to atmospheric pressure immediately crushes the can.

Measuring Pressure

A **barometer** *is a device used to measure atmospheric pressure.* The first type of barometer, illustrated in Figure 10-7, was introduced by Evangelista Torricelli during the early 1600s. Torricelli wondered why water pumps could raise water to a maximum height of only about 34 feet. He thought that the height must depend somehow on the weight of water compared with the weight of air. He reasoned that liquid mercury, which is about 14 times as dense as water, could be raised only 1/14 as high as water. To test this idea, Torricelli sealed a long glass tube at one end and filled it with mercury. Holding the open end with his thumb, he inverted the tube into a dish of mercury without allowing any air to enter the tube. When he removed his thumb, the mercury column in the tube dropped to a height of about 30 in. (760 mm) above the surface of the mercury in the dish. He repeated the experiment with tubes of different diameters and lengths longer than 760 mm. In every case, the mercury dropped to a height of about 760 mm.

The space above the mercury in such a tube is nearly a vacuum. The mercury in the tube pushes downward because of gravitational force. The column of mercury in the tube is stopped from falling beyond a certain point because the atmosphere exerts a pressure on the surface of the mercury outside the tube. This pressure is transmitted through the fluid mercury and is exerted upward on the column of mercury. The mercury in the tube falls only until the pressure exerted by its weight is equal to the pressure exerted by the atmosphere.

The exact height of the mercury in the tube depends on the atmospheric pressure, or force per unit area. The pressure is measured directly in terms of the height of the mercury column supported in the barometer tube.

From experiments like Torricelli's, it is known that at sea level at 0°C, the average pressure of the atmosphere can support a 760 mm column of mercury. At any given place on Earth, the specific atmospheric pressure depends on the elevation and the weather conditions at the time. If the atmospheric pressure is greater than the average at sea level, the height of the mercury column in a barometer will be greater than 760 mm. If the atmospheric pressure is less, the height of the mercury column will be less than 760 mm.

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All gases, not only those in the atmosphere, exert pressure. A device called a manometer can be used to measure the pressure of an enclosed gas sample, as shown in Figure 10-8. The difference in the height of mercury in the two arms of the U-tube is a measure of the oxygen gas pressure in the container.

Units of Pressure

A number of different units are used to measure pressure. Because atmospheric pressure is often measured by a mercury barometer, pressure can be expressed in terms of the height of a mercury column. *Thus, a common unit of pressure is* **millimeters of mercury,** *symbolized mm Hg. A pressure of 1 mm Hg is now called 1* **torr** in honor of Torricelli for his invention of the barometer. The average atmospheric pressure at sea level at 0°C is 760 mm Hg.

Pressures are often measured in units of atmospheres. *One* **atmosphere of pressure** *(atm) is defined as being exactly equivalent to 760 mm Hg.*

In SI, pressure is expressed in derived units called pascals. The unit is named for Blaise Pascal, a French mathematician and philosopher who studied pressure during the seventeenth century. *One* **pascal** *(Pa) is defined as the pressure exerted by a force of one newton (1 N) acting on an area of one square meter.*

In many cases, it is more convenient to express pressure in kilopascals (kPa). The standard atmosphere (1 atm) is equal to $1.013\,25 \times 10^5$ Pa, or 101.325 kPa. The pressure units used in this book are summarized in Table 10-1.

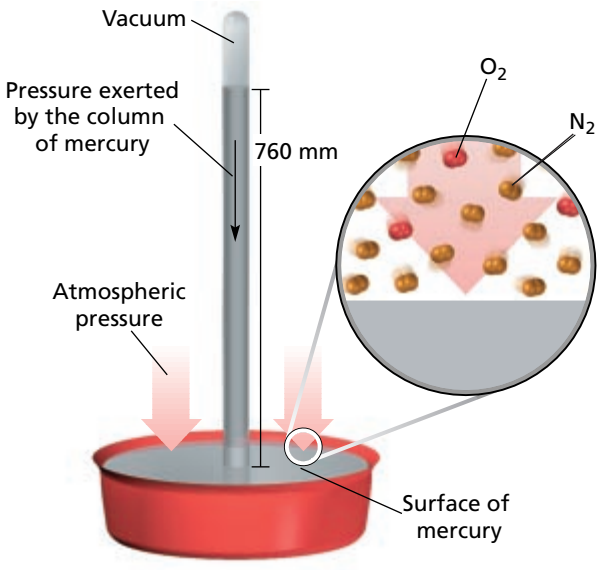

FIGURE 10-7 Torricelli discovered that the pressure of the atmosphere supports a column of mercury about 760 mm above the surface of the mercury in the dish.

TABLE 10-1 *Units of Pressure*

Unit	Symbol	Definition/relationship
pascal	Pa	SI pressure unit $1\ \text{Pa} = \frac{1\ \text{N}}{\text{m}^2}$
millimeter of mercury	mm Hg	pressure that supports a 1 mm mercury column in a barometer
torr	torr	1 torr = 1 mm Hg
atmosphere	atm	average atmospheric pressure at sea level and 0°C 1 atm = 760 mm Hg = 760 torr = $1.013\,25 \times 10^5$ Pa = 101.325 kPa

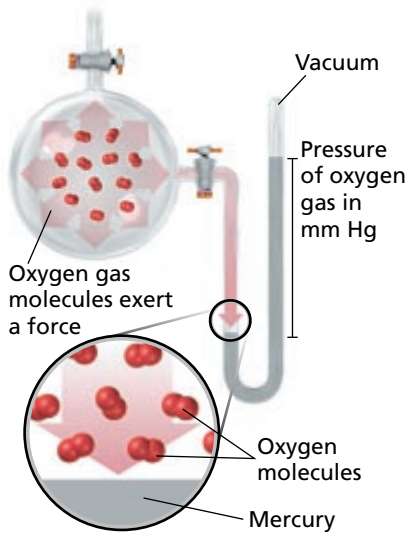

FIGURE 10-8 In the manometer above, the pressure of the oxygen gas in the flask pushes on the mercury column. The difference in the height of the mercury in the two arms of the U-tube indicates the oxygen gas pressure.

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Standard Temperature and Pressure

To compare volumes of gases, it is necessary to know the temperature and pressure at which the volumes are measured. *For purposes of comparison, scientists have agreed on standard conditions of exactly 1 atm pressure and 0°C. These conditions are called* **standard temperature and pressure** *and are commonly abbreviated STP.*

SAMPLE PROBLEM 10-1

The average atmospheric pressure in Denver, Colorado, is 0.830 atm. Express this pressure (a) in mm Hg and (b) in kPa.

SOLUTION

1 ANALYZE

Given: P of atmosphere = 0.830 atm

760 mm Hg = 1 atm (definition); 101.325 kPa = 1 atm (definition)

Unknown: **a.** P of atmosphere in mm Hg; **b.** P of atmosphere in kPa

2 PLAN

a. $\text{atm} \longrightarrow \text{mm Hg}$; $\text{atm} \times \dfrac{\text{mm Hg}}{\text{atm}} = \text{mm Hg}$

b. $\text{atm} \longrightarrow \text{kPa}$; $\text{atm} \times \dfrac{\text{kPa}}{\text{atm}} = \text{kPa}$

3 COMPUTE

a. $0.830\ \cancel{\text{atm}} \times \dfrac{760\ \text{mm Hg}}{\cancel{\text{atm}}} = 631\ \text{mm Hg}$

b. $0.830\ \cancel{\text{atm}} \times \dfrac{101.325\ \text{kPa}}{\cancel{\text{atm}}} = 84.1\ \text{kPa}$

4 EVALUATE

Units have canceled to give the desired units, and answers are properly expressed to the correct number of significant figures. The known pressure is roughly 80% of atmospheric pressure. The results are therefore reasonable because each is roughly 80% of the pressure as expressed in the new units.

PRACTICE

1. Convert a pressure of 1.75 atm to kPa and to mm Hg.

   Answer
   177 kPa, 1330 mm Hg

2. Convert a pressure of 570. torr to atmospheres and to kPa.

   Answer
   0.750 atm, 76.0 kPa

SECTION REVIEW

1. Define *pressure.*
2. What units are used to express pressure measurements?
3. What are standard conditions for gas measurements?
4. Convert the following pressures to pressures in standard atmospheres:
   a. 151.98 kPa
   b. 456 torr
   c. 912 mm Hg

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The Gas Laws

SECTION 10-3

Objectives

- Use the kinetic-molecular theory to explain the relationships between gas volume, temperature, and pressure.
- Use Boyle's law to calculate volume-pressure changes at constant temperature.
- Use Charles's law to calculate volume-temperature changes at constant pressure.
- Use Gay-Lussac's law to calculate pressure-temperature changes at constant volume.
- Use the combined gas law to calculate volume-temperature-pressure changes.
- Use Dalton's law of partial pressures to calculate partial pressures and total pressures.

Scientists have been studying physical properties of gases for hundreds of years. In 1662, Robert Boyle discovered that gas pressure and volume are related mathematically. The observations of Boyle and others led to the development of the gas laws. *The* **gas laws** *are simple mathematical relationships between the volume, temperature, pressure, and amount of a gas.*

Boyle's Law: Pressure-Volume Relationship

Robert Boyle discovered that doubling the pressure on a sample of gas at constant temperature reduces its volume by one-half. Tripling the gas pressure reduces its volume to one-third of the original. Reducing the pressure on a gas by one-half allows the volume of the gas to double. As one variable increases, the other decreases. Figure 10-9 shows that as the volume of gas in the syringe decreases, the pressure of the gas increases.

You can use the kinetic-molecular theory to understand why this pressure-volume relationship holds. The pressure of a gas is caused by

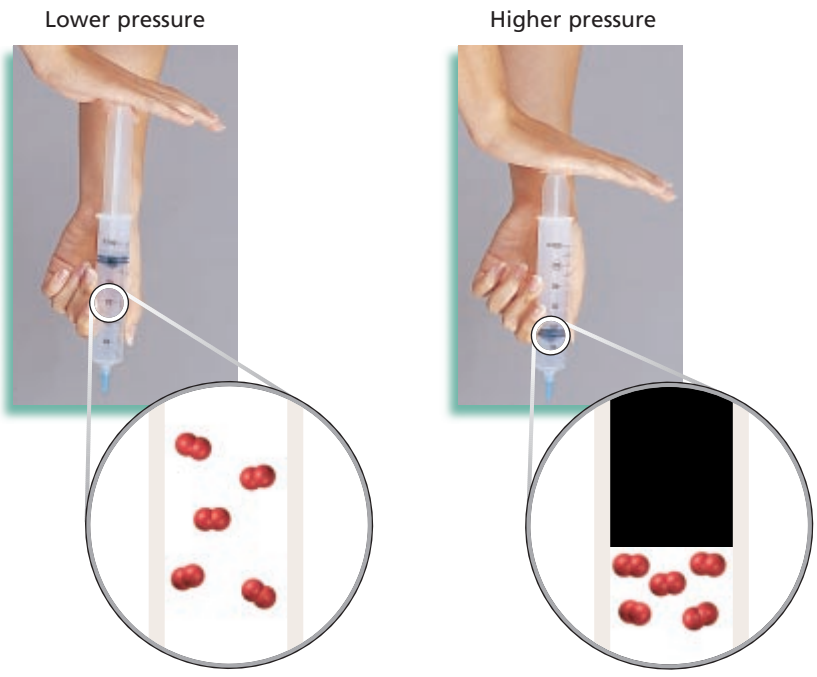

FIGURE 10-9 The volume of gas in the syringe shown in the photo is reduced when the plunger is pushed down. The gas pressure increases as the volume is reduced because the molecules collide more frequently with the walls of the container in a smaller volume.

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TABLE 10-2 *Volume-Pressure Data for a Gas Sample (at Constant Mass and Temperature)*

Volume (mL)	Pressure (atm)	$P \times V$
1200	0.5	600
600	1.0	600
300	2.0	600
200	3.0	600
150	4.0	600
120	5.0	600
100	6.0	600

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moving molecules hitting the container walls. Suppose the volume of a container is decreased but the same number of gas molecules is present at the same temperature. There will be more molecules per unit volume. The number of collisions with a given unit of wall area will increase as a result. Therefore, pressure will also increase.

Table 10-2 shows pressure and volume data for a constant mass of gas at constant temperature. Plotting the values of volume versus pressure gives a curve like that in Figure 10-10. The general volume-pressure relationship that is illustrated is called Boyle's law. **Boyle's law** *states that the volume of a fixed mass of gas varies inversely with the pressure at constant temperature.*

Mathematically, Boyle's law is expressed as follows.

$$V = k\frac{1}{P} \quad \text{or} \quad PV = k$$

The value of k is constant for a given sample of gas and depends only on the mass of gas and the temperature. (Note that for the data in Table 10-2, $k = 600$ mL•atm.) If the pressure of a given gas sample at constant temperature changes, the volume will change. However, the quantity *pressure times volume* will remain equal to the same value of k.

Boyle's law can be used to compare changing conditions for a gas. Using P_1 and V_1 to stand for initial conditions and P_2 and V_2 to stand for new conditions results in the following equations.

$$P_1V_1 = k \qquad P_2V_2 = k$$

Two quantities that are equal to the same thing are equal to each other.

$$P_1V_1 = P_2V_2$$

Given three of the four values P_1, V_1, P_2, and V_2, you can use this equation to calculate the fourth value for a system at constant temperature. For example, suppose that 1.0 L of gas is initially at 1.0 atm pressure (V_1 = 1.0 L, P_1 = 1.0 atm). The gas is allowed to expand fivefold at constant temperature to 5.0 L (V_2 = 5.0 L). You can then calculate the new pressure, P_2, by rearranging the equation as follows.

Volume vs. Pressure for a Gas at Constant Temperature

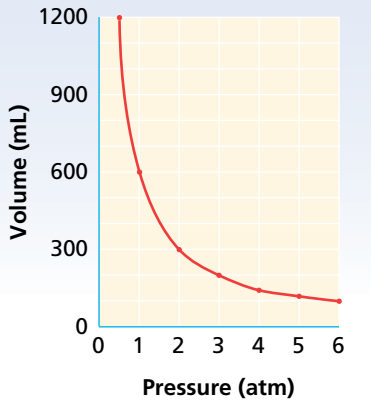

FIGURE 10-10 This graph shows that there is an inverse relationship between volume and pressure. As the pressure drops by half, the volume doubles.

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$$P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{(1.0 \text{ atm})(1.0 \text{ L})}{5.0 \text{ L}} = 0.20 \text{ atm}$$

The pressure has decreased to one-fifth the original pressure, while the volume increased fivefold.

SAMPLE PROBLEM 10-2

A sample of oxygen gas has a volume of 150. mL when its pressure is 0.947 atm. What will the volume of the gas be at a pressure of 0.987 atm if the temperature remains constant?

SOLUTION

1 ANALYZE

Given: V_1 of $O_2 = 150.$ mL
P_1 of $O_2 = 0.947$ atm; P_2 of $O_2 = 0.987$ atm
Unknown: V_2 of O_2 in mL

2 PLAN

$$P_1, V_1, P_2 \longrightarrow V_2$$

Rearrange the equation for Boyle's law ($P_1V_1 = P_2V_2$) to obtain V_2.

$$V_2 = \frac{P_1 V_1}{P_2}$$

3 COMPUTE

Substitute values for P_1, V_1, and P_2 to obtain the new volume, V_2.

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(0.947 \cancel{\text{atm}})(150. \text{ mL } O_2)}{0.987 \cancel{\text{atm}}} = 144 \text{ mL } O_2$$

4 EVALUATE

When the pressure is increased slightly at constant temperature, the volume decreases slightly, as expected. Units cancel to give milliliters, a volume unit.

PRACTICE

1. A balloon filled with helium gas has a volume of 500 mL at a pressure of 1 atm. The balloon is released and reaches an altitude of 6.5 km, where the pressure is 0.5 atm. Assuming that the temperature has remained the same, what volume does the gas occupy at this height?

   Answer 1000 mL He

2. A gas has a pressure of 1.26 atm and occupies a volume of 7.40 L. If the gas is compressed to a volume of 2.93 L, what will its pressure be, assuming constant temperature?

   Answer 3.18 atm

3. Divers know that the pressure exerted by the water increases about 100 kPa with every 10.2 m of depth. This means that at 10.2 m below the surface, the pressure is 201 kPa; at 20.4 m, the pressure is 301 kPa; and so forth. Given that the volume of a balloon is 3.5 L at STP and that the temperature of the water remains the same, what is the volume 51 m below the water's surface?

   Answer 0.59 L

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Charles's Law: Volume-Temperature Relationship

Balloonists, such as those in the photo at the beginning of this chapter, are making use of a physical property of gases: if pressure is constant, gases expand when heated. When the temperature increases, the volume of a fixed number of gas molecules must increase if the pressure is to stay constant. At the higher temperature, the gas molecules move faster. They collide with the walls of the container more frequently and with more force. The increased pressure causes the volume of a flexible container to increase; then the molecules must travel farther before reaching the walls. The rate of collisions against each unit of wall area decreases. This lower collision frequency offsets the greater collision force at the higher temperature. The pressure thus stays constant.

The quantitative relationship between volume and temperature was discovered by the French scientist Jacques Charles in 1787. Charles's experiments showed that all gases expand to the same extent when heated through the same temperature interval. Charles found that the volume changes by 1/273 of the original volume for each Celsius degree, at constant pressure and an initial temperature of 0°C. For example, raising the temperature to 1°C causes the gas volume to increase by 1/273 of the volume it had at 0°C. A 10°C temperature increase causes the volume to expand by 10/273 of the original volume at 0°C. If the temperature is increased by 273°C, the volume increases by 273/273 of the original, that is, the volume doubles.

The same regularity of volume change occurs if a gas is cooled at constant pressure, as the balloons in Figure 10-11 show. At 0°C, a 1°C decrease in temperature decreases the original volume by 1/273. At this rate of volume decrease, a gas cooled from 0°C to –273°C would be decreased by 273/273. In other words, it would have zero volume, which

FIGURE 10-11 As air-filled balloons are exposed to liquid nitrogen, they shrink greatly in volume. When they are removed from the liquid nitrogen and the air inside them is warmed to room temperature, the balloons expand to their original volume.

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TABLE 10-3 ***Volume-Temperature Data for a Gas Sample (at Constant Mass and Pressure)***

Temperature (°C)	Volume (mL)
273	1092
100	746
10	566
1	548
0	546
–1	544
–73	400
–173	200
–223	100

is not actually possible. In fact, real gases cannot be cooled to –273°C. Before they reach that temperature, intermolecular forces exceed the kinetic energy of the molecules, and the gases condense to form liquids or solids.

The data in Table 10-3 illustrate the temperature-volume relationship at constant pressure for a gas sample with a volume of 546 mL at 0°C. When the gas is warmed by 1°C, it expands by 1/273 its original volume. In this case, each 1°C temperature change from 0°C causes a volume change of 2 mL, or 1/273 of 546 mL. Raising the temperature to 100°C from 0°C increases the volume by 200 mL, or 100/273 of 546 mL.

Note that in Table 10-3, the volume does not increase in direct proportion to the Celsius temperature. For example, notice what happens when the temperature is increased tenfold from 10°C to 100°C. The volume does not increase tenfold but increases only from 566 mL to 746 mL.

The Kelvin temperature scale is a scale that starts at a temperature corresponding to –273.15°C. That temperature is the lowest one possible. *The temperature –273.15°C is referred to as* **absolute zero** *and is given a value of zero in the Kelvin scale.* This fact gives the following relationship between the two temperature scales.

$$K = 273.15 + °C$$

For calculations in this book, 273.15 is rounded off to 273.

The average kinetic energy of gas molecules is more closely related to the Kelvin temperature. Gas volume and Kelvin temperature are directly proportional to each other. For example, quadrupling the Kelvin temperature causes the volume of a gas to quadruple, and reducing the Kelvin temperature by half causes the volume of a gas to decrease by half.

The relationship between Kelvin temperature and gas volume is known as Charles's law. **Charles's law** *states that the volume of a fixed mass of gas at constant pressure varies directly with the Kelvin temperature.*

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TABLE 10-4 Volume-Temperature Data for a Gas Sample (at Constant Mass and Pressure)

Volume (mL)	Kelvin temperature (K)	V/T or k (mL/K)
1092	546	2
746	373	2
566	283	2
548	274	2
546	273	2
544	272	2
400	200	2
100	50	2

Volume vs. Temperature for a Gas at Constant Pressure

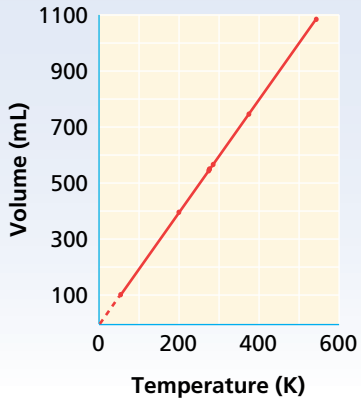

FIGURE 10-12 This graph shows the plot of the volume versus the Kelvin temperature data from Table 10-4. It gives a straight line that, when extended, indicates the volume will become 0 at –273°C. Such a plot is characteristic of directly proportional variables.

Figure 10-12 illustrates the relationship between gas volume and Kelvin temperature by plotting the data from Table 10-4. Charles's law may be expressed as follows.

$$V = kT \quad \text{or} \quad \frac{V}{T} = k$$

The value of T is the Kelvin temperature, and k is a constant. The value of k depends only on the quantity of gas and the pressure. The ratio V/T for any set of volume-temperature values always equals the same k. The form of Charles's law that can be applied directly to most volume-temperature problems involving gases is as follows.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

V_1 and T_1 represent initial conditions. V_2 and T_2 represent a new set of conditions. When three of the four values V_1, T_1, V_2, and T_2 are known, this equation can be used to calculate the fourth value.

SAMPLE PROBLEM 10-3

A sample of neon gas occupies a volume of 752 mL at 25°C. What volume will the gas occupy at 50°C if the pressure remains constant?

SOLUTION

1 *ANALYZE*

Given: V_1 of Ne = 752 mL

T_1 of Ne = 25°C + 273 = 298 K; T_2 of Ne = 50°C + 273 = 323 K

Note that Celsius temperatures have been converted to kelvins. This is a *very important* step for working the problems in this chapter.

Unknown: V_2 of Ne in mL

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2 PLAN Because the gas remains at constant pressure, an increase in temperature will cause an increase in volume. To obtain V_2, rearrange the equation for Charles's law.

$$V_2 = \frac{V_1 T_2}{T_1}$$

3 COMPUTE Substitute values for V_1, T_1, and T_2 to obtain the new volume, V_2.

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(752 \text{ mL Ne})(323 \cancel{\text{K}})}{298 \cancel{\text{K}}} = 815 \text{ mL Ne}$$

4 EVALUATE As expected, the volume of the gas increases as the temperature increases. Units cancel to yield milliliters, as desired. The answer contains the appropriate number of significant figures. It is also reasonably close to an estimated value of 812, calculated as $(750 \times 325)/300$.

PRACTICE

1. A helium-filled balloon has a volume of 2.75 L at 20.°C. The volume of the balloon decreases to 2.46 L after it is placed outside on a cold day. What is the outside temperature in K? in °C?

   Answer 262 K, or –11°C

2. A gas at 65°C occupies 4.22 L. At what Celsius temperature will the volume be 3.87 L, assuming the same pressure?

   Answer 37°C

Gay-Lussac's Law: Pressure-Temperature Relationship

You have just learned about the quantitative relationship between volume and temperature at constant pressure. What would you predict about the relationship between pressure and temperature at constant volume? You have seen that pressure is the result of collisions of molecules with container walls. The energy and frequency of collisions depend on the average kinetic energy of molecules, which depends on temperature. For a fixed quantity of gas at constant volume, the pressure should be directly proportional to the Kelvin temperature, which depends directly on average kinetic energy.

That prediction turns out to be correct. For every kelvin of temperature change, the pressure of a confined gas changes by 1/273 of the pressure at 0°C. Joseph Gay-Lussac is given credit for recognizing this in 1802. The data plotted in Figure 10-13 illustrate **Gay-Lussac's law:** *The pressure of a fixed mass of gas at constant volume varies directly with the Kelvin temperature.* Mathematically, Gay-Lussac's law is expressed as follows.

$$P = kT \quad \text{or} \quad \frac{P}{T} = k$$

Pressure vs. Temperature for a Gas at Constant Volume

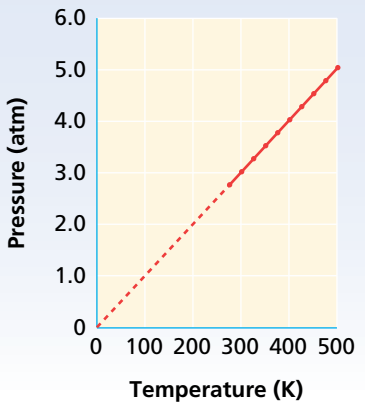

FIGURE 10-13 This graph shows that gas pressure varies directly with Kelvin temperature at constant volume.

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The value of T is the temperature in kelvins, and k is a constant that depends on the quantity of gas and the volume. For a given mass of gas at constant volume, the ratio P/T is the same for any set of pressure-temperature values. Unknown values can be found using this form of Gay-Lussac's law.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

When values are known for three of the four quantities, the fourth value can be calculated.

SAMPLE PROBLEM 10-4

The gas in an aerosol can is at a pressure of 3.00 atm at 25°C. Directions on the can warn the user not to keep the can in a place where the temperature exceeds 52°C. What would the gas pressure in the can be at 52°C?

SOLUTION

1 ANALYZE

Given: P_1 of gas = 3.00 atm

T_1 of gas = 25°C + 273 = 298 K; T_2 of gas = 52°C + 273 = 325 K

Unknown: P_2 of gas in atm

2 PLAN

Because the gaseous contents remain at the constant volume of the can, an increase in temperature will cause an increase in pressure. Rearrange Gay-Lussac's law to obtain P_2.

$$P_2 = \frac{P_1 T_2}{T_1}$$

3 COMPUTE

Substitute values for P_1, T_2, and T_1 to obtain the new pressure, P_2.

$$P_2 = \frac{(3.00 \text{ atm})(325 \cancel{\text{K}})}{298 \cancel{\text{K}}} = 3.27 \text{ atm}$$

4 EVALUATE

As expected, a temperature increase at constant volume causes the pressure of the contents in the can to increase. Units cancel correctly. The answer contains the proper number of significant figures. It also is reasonably close to an estimated value of 3.25, calculated as $(3 \times 325)/300$.

PRACTICE

1. Before a trip from New York to Boston, the pressure in an automobile tire is 1.8 atm at 20.°C. At the end of the trip, the pressure gauge reads 1.9 atm. What is the new Celsius temperature of the air inside the tire? (Assume tires with constant volume.)

   Answer 36°C

2. At 120.°C, the pressure of a sample of nitrogen is 1.07 atm. What will the pressure be at 205°C, assuming constant volume?

   Answer 1.30 atm

3. A sample of helium gas has a pressure of 1.20 atm at 22°C. At what Celsius temperature will the helium reach a pressure of 2.00 atm?

   Answer 219°C

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The Combined Gas Law

A gas sample often undergoes changes in temperature, pressure, and volume all at the same time. When this happens, three variables must be dealt with at once. Boyle's law, Charles's law, and Gay-Lussac's law can be combined into a single expression that is useful in such situations. *The* **combined gas law** *expresses the relationship between pressure, volume, and temperature of a fixed amount of gas.* The combined gas law can be expressed as follows.

$$\frac{PV}{T} = k$$

In the equation, k is constant and depends on the amount of gas. The combined gas law can also be written as follows.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The subscripts in the equation above indicate two different sets of conditions, and T represents Kelvin temperature. From this expression, any value can be calculated if the other five are known. Note that each of the individual gas laws can be obtained from the combined gas law when the proper variable is constant. Thus, when temperature is constant, T can be canceled out of both sides of the general equation because it represents the same value ($T_1 = T_2$). This leaves Boyle's law.

$$P_1V_1 = P_2V_2$$

If the pressure is held constant, P will cancel out of both sides of the general equation, since $P_1 = P_2$. Charles's law is obtained.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Keeping the volume constant means V can be canceled out of both sides of the general equation because $V_1 = V_2$. This gives Gay-Lussac's law.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

SAMPLE PROBLEM 10-5

A helium-filled balloon has a volume of 50.0 L at 25°C and 1.08 atm. What volume will it have at 0.855 atm and 10.°C?

SOLUTION

1 *ANALYZE*

Given: V_1 of He = 50.0 L
T_1 of He = 25°C + 273 = 298 K; T_2 of He = 10°C + 273 = 283 K
P_1 of He = 1.08 atm; P_2 of He = 0.855 atm

Unknown: V_2 of He in L

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2 PLAN Because the gas changes in both temperature and pressure, the combined gas law is needed. Rearrange the combined gas law to solve for the final volume, V_2.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \longrightarrow V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

3 COMPUTE Substitute the known values into the equation to obtain a value for V_2.

$$V_2 = \frac{(1.08\ \cancel{\text{atm}})(50.0\text{ L He})(283\ \cancel{\text{K}})}{(0.855\ \cancel{\text{atm}})(298\ \cancel{\text{K}})} = 60.0\text{ L He}$$

4 EVALUATE Here the pressure decreases much more than the temperature decreases. As expected, the net result of the two changes gives an increase in the volume, from 50.0 L to 60.0 L. Units cancel appropriately. The answer is correctly expressed to three significant figures. It is also reasonably close to an estimated value of 50, calculated as $(50 \times 300)/300$.

PRACTICE

1. The volume of a gas is 27.5 mL at 22.0°C and 0.974 atm. What will the volume be at 15.0°C and 0.993 atm?

Answer
26.3 mL

2. A 700. mL gas sample at STP is compressed to a volume of 200. mL, and the temperature is increased to 30.0°C. What is the new pressure of the gas in Pa?

Answer
3.94×10^5 Pa, or 394 kPa

Dalton's Law of Partial Pressures

John Dalton, the English chemist who proposed the atomic theory, also studied gas mixtures. He found that *in the absence of a chemical reaction*, the pressure of a gas mixture is the sum of the individual pressures of each gas alone. Figure 10-14 shows a 1.0 L container filled with oxygen gas at a pressure of 0.12 atm at 0°C. In another 1.0 L container, an equal number of molecules of nitrogen gas exert a pressure of 0.12 atm at 0°C. The gas samples are then combined in a 1.0 L container. (At 0°C, oxygen gas and nitrogen gas are unreactive.) The total pressure of the mixture is found to be 0.24 atm at 0°C. The pressure that each gas exerts in the mixture is independent of that exerted by other gases present. *The pressure of each gas in a mixture is called the* **partial pressure** *of that gas.* **Dalton's law of partial pressures** *states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the component gases.* The law is true regardless of the number of different gases that are present. Dalton's law may be expressed as follows.

$$P_T = P_1 + P_2 + P_3 + \ldots$$

P_T is the total pressure of the mixture. $P_1, P_2, P_3, \ldots$ are the partial pressures of component gases 1, 2, 3, and so on.

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You can understand Dalton's law in terms of the kinetic-molecular theory. The rapidly moving particles of each gas in a mixture have an equal chance to collide with the container walls. Therefore, each gas exerts a pressure independent of that exerted by the other gases present. The total pressure is the result of the total number of collisions per unit of wall area in a given time. (Note that because gas particles move independently, the other gas laws, as well as Dalton's law, can be applied to unreacting gas mixtures.)

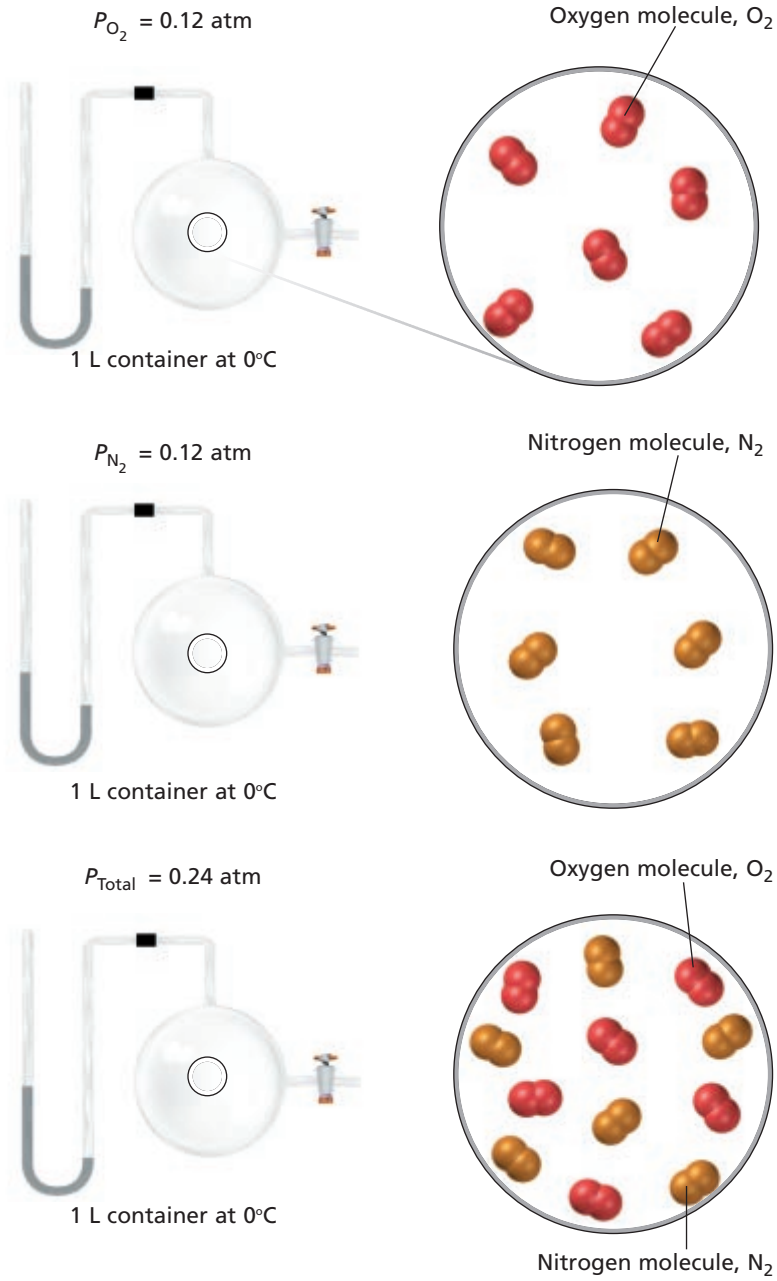

FIGURE 10-14 Samples of oxygen gas and nitrogen gas are mixed. The total pressure of the mixture is the sum of the pressures of the gases.

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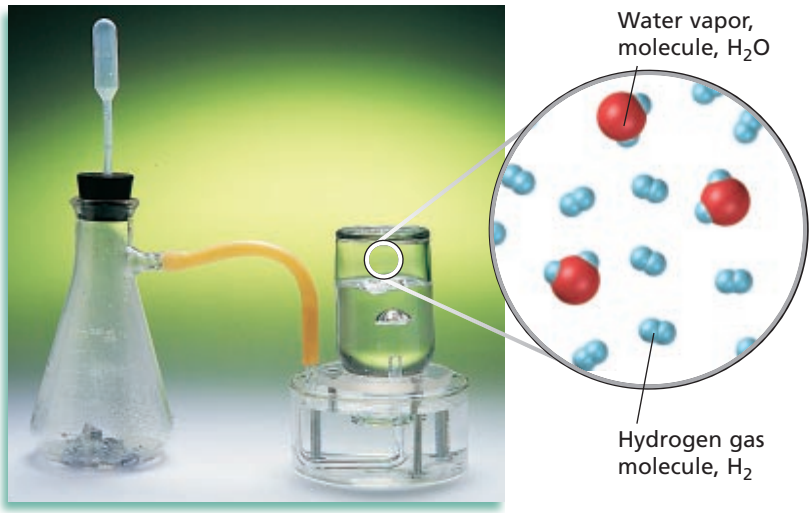
FIGURE 10-15
Hydrogen can be collected by water displacement by reacting zinc with sulfuric acid. The hydrogen gas produced displaces the water in the gas collecting bottle. It now contains some water vapor.



Gases Collected by Water Displacement

Gases produced in the laboratory are often collected over water, as shown in Figure 10-15. The gas produced by the reaction displaces the water, which is more dense, in the collection bottle. You can apply Dalton's law of partial pressures in calculating the pressures of gases collected in this way. A gas collected by water displacement is not pure but is always mixed with water vapor. That is because water molecules at the liquid surface evaporate and mix with the gas molecules. Water vapor, like other gases, exerts a pressure, known as *water-vapor pressure*.

Suppose you wished to determine the total pressure of the gas and water vapor inside a collection bottle. You would raise the bottle until the water levels inside and outside the bottle were the same. At that point, the total pressure inside the bottle would be the same as the atmospheric pressure, P_{atm}. According to Dalton's law of partial pressures, the following is true.

$$P_{atm} = P_{gas} + P_{H_2O}$$

Suppose you then needed to calculate the partial pressure of the dry gas collected. You would read the atmospheric pressure, P_{atm}, from a barometer in the laboratory. To make the calculation, subtract the vapor pressure of the water at the given temperature from the total pressure. The vapor pressure of water varies with temperature. You need to look up the value of P_{H_2O} at the temperature of the experiment in a standard reference table like that in Table A-8 of this book.

SAMPLE PROBLEM 10-6

Oxygen gas from the decomposition of potassium chlorate, $KClO_3$, was collected by water displacement. The barometric pressure and the temperature during the experiment were 731.0 torr and 20.0°C, respectively. What was the partial pressure of the oxygen collected?

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SOLUTION

1 ANALYZE

Given: $P_T = P_{atm} = 731.0$ torr

$P_{H_2O} = 17.5$ torr (vapor pressure of water at 20.0°C, from Table A-8)

$P_{atm} = P_{O_2} + P_{H_2O}$

Unknown: P_{O_2} in torr

2 PLAN

The partial pressure of the collected oxygen is found by subtracting the partial pressure of water vapor from the atmospheric pressure, according to Dalton's law of partial pressures.

$$P_{O_2} = P_{atm} - P_{H_2O}$$

3 COMPUTE

Substituting values for P_{atm} and P_{H_2O} gives P_{O_2}.

$$P_{O_2} = 731.0 \text{ torr} - 17.5 \text{ torr} = 713.5 \text{ torr}$$

4 EVALUATE

As expected, the oxygen partial pressure is less than atmospheric pressure. It is also much larger than the partial pressure of water vapor at this temperature. The answer has the appropriate number of significant figures. It is reasonably close to an estimated value of 713, calculated as 730 – 17.

PRACTICE

1. Some hydrogen gas is collected over water at 20.0°C. The levels of water inside and outside the gas-collection bottle are the same. The partial pressure of hydrogen is 742.5 torr. What is the barometric pressure at the time the gas is collected?

   Answer 760.0 torr

2. Helium gas is collected over water at 25°C. What is the partial pressure of the helium, given that the barometric pressure is 750.0 mm Hg?

   Answer 726.2 mm Hg

SECTION REVIEW

1. State Boyle's law, Charles's law, and the combined gas law in mathematical terms.
2. A sample of helium gas has a volume of 200.0 mL at 0.960 atm. What pressure, in atm, is needed to reduce the volume at constant temperature to 50.0 mL?
3. A certain quantity of gas has a volume of 0.750 L at 298 K. At what temperature, in degrees Celsius, would this quantity of gas be reduced to 0.500 L, assuming constant pressure?
4. An aerosol can contains gases under a pressure of 4.50 atm at 20.0°C. If the can is left on a hot, sandy beach, the pressure of the gases increases to 4.80 atm. What is the Celsius temperature on the beach?
5. Discuss the significance of the absolute-zero temperature.
6. A certain mass of oxygen was collected over water when potassium chlorate was decomposed by heating. The volume of the oxygen sample collected was 720. mL at 25.0°C and a barometric pressure of 755 torr. What would the volume of the oxygen be at STP? (Hint: First calculate the partial pressure of the oxygen, using Appendix Table A-8. Then use the combined gas law.)

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CHAPTER 10 REVIEW

CHAPTER SUMMARY

10-1

- The kinetic-molecular theory of matter can be used to explain the properties of gases, liquids, and solids.
- The kinetic-molecular theory of gases describes a model of an ideal gas. The behavior of most gases is close to ideal except at very high pressures and low temperatures.
- Gases consist of large numbers of tiny, fast-moving particles that are far apart relative to their size. The average kinetic energy of the particles depends on the temperature of the gas.
- Gases exhibit expansion, fluidity, low density, compressibility, diffusion, and effusion.

Vocabulary

diffusion (305)
effusion (306)
elastic collision (303)
fluids (305)
ideal gas (303)
kinetic-molecular theory (303)
real gas (306)

10-2

- Conditions of standard temperature and pressure (STP) allow comparison of volumes of different gases.
- Pressure, volume, temperature, and number of molecules are the four measureable quantities needed to fully describe a gas.
- The gas molecules that make up the atmosphere exert pressure against Earth's surface, varying with weather conditions and elevation.
- A barometer measures the pressure of the atmosphere. The pressure of a gas in a closed container can be measured by a manometer.

Vocabulary

atmosphere of pressure (311)
barometer (310)
millimeters of mercury (311)
newton (309)
pascal (311)
pressure (308)
standard temperature and pressure (312)
torr (311)

10-3

- Boyle's law shows the inverse relationship between the volume and the pressure of a gas.

$$PV = k$$

- Charles's law illustrates the direct relationship between the volume of a gas and its temperature in kelvins.

$$V = kT$$

- Gay-Lussac's law represents the direct relationship between the pressure of a gas and its temperature in kelvins.

$$P = kT$$

- The combined gas law, as its name implies, combines the previous relationships into the following mathematical expression.

$$\frac{PV}{T} = k$$

- A gas exerts pressure on the walls of its container. In a mixture of unreacting gases, the total pressure equals the sum of the partial pressures of each gas.

Vocabulary

absolute zero (317)
Boyle's law (314)
Charles's law (317)
combined gas law (321)
Dalton's law of partial pressures (322)
gas laws (313)
Gay-Lussac's law (319)
partial pressure (322)

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REVIEWING CONCEPTS

1. What idea is the kinetic-molecular theory based on? (10-1)
2. What is an ideal gas? (10-1)
3. State the five basic assumptions of the kinetic-molecular theory. (10-1)
4. How do gases compare with liquids and solids in terms of the distance between their molecules? (10-1)
5. What is an elastic collision? (10-1)
6. a. Write and label the equation that relates the average kinetic energy and speed of gas particles.
   b. What is the relationship between the temperature, speed, and kinetic energy of gas molecules? (10-1)
7. a. What is diffusion?
   b. What factors affect the rate of diffusion of one gas through another?
   c. What is the relationship between the mass of a gas particle and the rate at which it diffuses through another gas?
   d. What is effusion? (10-1)
8. a. Why does a gas in a closed container exert pressure?
   b. What is the relationship between the area a force is applied to and the resulting pressure? (10-2)
9. a. What is atmospheric pressure?
   b. Why does the atmosphere exert pressure?
   c. What is the value of atmospheric pressure at sea level, in newtons per square centimeter? (10-2)
10. a. Why does a column of mercury in a tube that is inverted in a dish of mercury have a height of about 760 mm at sea level?
    b. What height would be maintained by a column of water inverted in a dish of water at sea level?
    c. What accounts for the difference in the heights of the mercury and water columns? (10-2)
11. a. Identify three units used to express pressure.
    b. Convert one atmosphere to torr.
    c. What is a pascal?
    d. What is the SI equivalent of one standard atmosphere of pressure? (10-2)
12. a. At constant pressure, how does temperature relate to the volume of a given quantity of gas?
    b. How does this explain the danger of throwing an aerosol can into a fire? (10-3)
13. a. What is the Celsius equivalent of absolute zero?
    b. What is the significance of this temperature?
    c. What is the relationship between Kelvin temperature and the average kinetic energy of gas molecules? (10-3)
14. a. Explain what is meant by the partial pressure of each gas within a mixture of gases.
    b. How do the partial pressures of gases in a mixture affect each other? (10-3)

PROBLEMS

Pressure and Temperature Conversions

15. If the atmosphere can support a column of mercury 760 mm high at sea level, what height (in mm) of each of the following could be supported, given the relative density values cited?
    a. water, whose density is approximately 1/14 that of mercury
    b. a hypothetical liquid with a density 1.40 times that of mercury
16. Convert each of the following into a pressure reading expressed in torr. (Hint: See Sample Problem 10-1.)
    a. 1.25 atm
    b. 2.48×10^{-3} atm
    c. 4.75×10^{4} atm
    d. 7.60×10^{6} atm
17. Convert each of the following into the unit specified.
    a. 125 mm Hg into atm
    b. 3.20 atm into Pa
    c. 5.38 kPa into torr
18. Convert each of the following Celsius temperatures to Kelvin temperatures.
    a. 0.°C
    b. 27°C
    c. –50.°C
    d. –273°C
19. Convert each of the following Kelvin temperatures to Celsius temperatures.
    a. 273 K
    b. 350. K
    c. 100. K
    d. 20. K

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Boyle's Law

20. Use Boyle's law to solve for the missing value in each of the following. (Hint: See Sample Problem 10-2.)
a. $P_1 = 350.$ torr, $V_1 = 200.$ mL, $P_2 = 700.$ torr, $V_2 = ?$
b. $P_1 = 0.75$ atm, $V_2 = 435$ mL, $P_2 = 0.48$ atm, $V_1 = ?$
c. $V_1 = 2.4 \times 10^5$ L, $P_2 = 180$ mm Hg, $V_2 = 1.8 \times 10^3$ L, $P_1 = ?$

21. The pressure exerted on a 240. mL sample of hydrogen gas at constant temperature is increased from 0.428 atm to 0.724 atm. What will the final volume of the sample be?

22. A flask containing 155 cm^3 of hydrogen was collected under a pressure of 22.5 kPa. What pressure would have been required for the volume of the gas to have been 90.0 cm^3, assuming the same temperature?

23. A gas has a volume of 450.0 mL. If the temperature is held constant, what volume would the gas occupy if the pressure were
a. doubled? (Hint: Express P_2 in terms of P_1.)
b. reduced to one-fourth of its original value?

24. A sample of oxygen that occupies 1.00×10^6 mL at 575 mm Hg is subjected to a pressure of 1.25 atm. What will the final volume of the sample be if the temperature is held constant?

Charles's Law

25. Use Charles's law to solve for the missing value in each of the following. (Hint: See Sample Problem 10-3.)
a. $V_1 = 80.0$ mL, $T_1 = 27°C$, $T_2 = 77°C$, $V_2 = ?$
b. $V_1 = 125$ L, $V_2 = 85.0$ L, $T_2 = 127°C$, $T_1 = ?$
c. $T_1 = -33°C$, $V_2 = 54.0$ mL, $T_2 = 160.°C$, $V_1 = ?$

26. A sample of air has a volume of 140.0 mL at 67°C. At what temperature will its volume be 50.0 mL at constant pressure?

27. At standard temperature, a gas has a volume of 275 mL. The temperature is then increased to 130.°C, and the pressure is held constant. What is the new volume?

Gay-Lussac's Law

28. A sample of hydrogen at 47°C exerts a pressure of 0.329 atm. The gas is heated to 77°C at constant volume. What will its new pressure be? (Hint: See Sample Problem 10-4.)

29. To what temperature must a sample of nitrogen at 27°C and 0.625 atm be taken so that its pressure becomes 1.125 atm at constant volume?

30. The pressure on a gas at –73°C is doubled, but its volume is held constant. What will the final temperature be in degrees Celsius?

Combined Gas Law

31. A sample of gas at 47°C and 1.03 atm occupies a volume of 2.20 L. What volume would this gas occupy at 107°C and 0.789 atm? (Hint: See Sample Problem 10-5.)

32. A 350. mL air sample collected at 35°C has a pressure of 550. torr. What pressure will the air exert if it is allowed to expand to 425 mL at 57°C?

33. A gas has a volume of 1.75 L at –23°C and 150. kPa. At what temperature would the gas occupy 1.30 L at 210. kPa?

34. A sample of oxygen at 40.°C occupies 820. mL. If this sample later occupies 1250 mL at 60.°C and 1.40 atm, what was its original pressure?

35. A gas at 7.75×10^4 Pa and 17°C occupies a volume of 850. cm^3. At what temperature, in degrees Celsius, would the gas occupy 720. cm^3 at 8.10×10^4 Pa?

36. A meteorological balloon contains 250. L of He at 22°C and 740. mm Hg. If the volume of the balloon can vary according to external conditions, what volume would it occupy at an altitude at which the temperature is –52°C and the pressure is 0.750 atm?

37. The balloon in the previous problem will burst if its volume reaches 400. L. Given the initial conditions specified in that problem, at what temperature, in degrees Celsius, will the balloon burst if its pressure at that bursting point is 0.475 atm?

38. The normal respiratory rate for a human being is 15.0 breaths per minute. The average volume

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of air for each breath is 505 cm^3 at 20.°C and 9.95×10^4 Pa. What is the volume of air at STP that an individual breathes in one day? Give your answer in cubic meters.

Dalton's Law of Partial Pressures

39. Three of the primary components of air are carbon dioxide, nitrogen, and oxygen. In a sample containing a mixture of only these gases at exactly one atmosphere pressure, the partial pressures of carbon dioxide and nitrogen are given as $P_{CO_2} = 0.285$ torr and $P_{N_2} = 593.525$ torr. What is the partial pressure of oxygen? (Hint: See Sample Problem 10-6.)

40. Determine the partial pressure of oxygen collected by water displacement if the water temperature is 20.0°C and the total pressure of the gases in the collection bottle is 730.0 torr.

41. A sample of gas is collected over water at a temperature of 35.0°C when the barometric pressure reading is 742.0 torr. What is the partial pressure of the dry gas?

42. A sample of oxygen is collected in a 175 mL container over water at 15°C, and the barometer reads 752.0 torr. What volume would the dry gas occupy at 770.0 torr and 15°C?

43. Suppose that 120. mL of argon is collected over water at 25°C and 780.0 torr. Compute the volume of the dry argon at STP.

MIXED REVIEW

44. A mixture of three gases, A, B, and C, is at a total pressure of 6.11 atm. The partial pressure of gas A is 1.68 atm; that of gas B is 3.89 atm. What is the partial pressure of gas C?

45. A child receives a balloon filled with 2.30 L of helium from a vendor at an amusement park. The temperature outside is 311 K. What will the volume of the balloon be when the child brings it home to an air-conditioned house at 295 K? Assume that the pressure stays the same.

46. A sample of argon gas occupies a volume of 295 mL at 36°C. What volume will the gas occupy at 55°C, assuming constant pressure?

47. A sample of carbon dioxide gas occupies 638 mL at 0.893 atm and 12°C. What will the pressure be at a volume of 881 mL and a temperature of 18°C?

48. At 84°C, a gas in a container exerts a pressure of 0.503 atm. Assuming the size of the container has not changed, at what Celsius temperature would the pressure be 1.20 atm?

49. A weather balloon at Earth's surface has a volume of 4.00 L at 304 K and 755 mm Hg. If the balloon is released and the volume reaches 4.08 L at 728 mm Hg, what is the temperature?

50. A gas has a pressure of 4.62 atm when its volume is 2.33 L. What will the pressure be when the volume is changed to 1.03 L, assuming constant temperature? Express the final pressure in torr.

51. At a deep-sea station 200. m below the surface of the Pacific Ocean, workers live in a highly pressurized environment. How many liters of gas at STP must be compressed on the surface to fill the underwater environment with 2.00×10^7 L of gas at 20.0 atm? Assume that temperature remains constant.

CRITICAL THINKING

52. Applying Models

a. Why do we say the graph in Figure 10-10 illustrates an inverse relationship?

b. Why does the data plotted in Figure 10-12 show a direct relationship?

53. Relating Ideas Explain how different gases in a mixture can have the same average kinetic energy value, even though the masses of their individual particles differ.

54. Inferring Conclusions If all gases behaved as ideal gases under all conditions of temperature and pressure, there would be no solid or liquid forms of these substances. Explain.

55. Relating Ideas Pressure is defined as force per unit area. Yet Torricelli found that the diameter of the barometer dish and the surface area of contact between the mercury in the tube and in the dish did not affect the height of mercury

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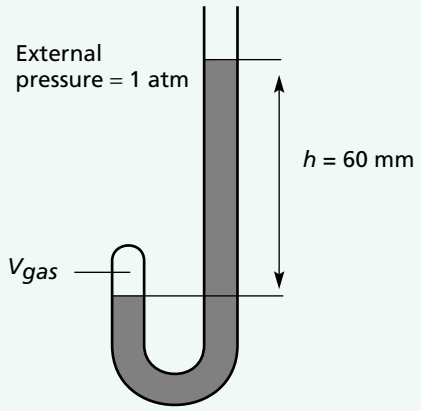
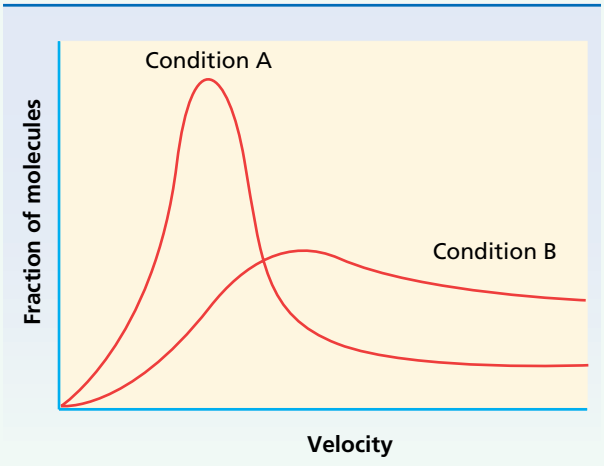
that was supported. Explain this seemingly inconsistent observation in view of the relationship between pressure and surface areas.

56. Interpreting Graphics Examine Boyle's J-tube apparatus shown here. The tube is open to the atmosphere at the top. The other end is closed and contains a gas with a volume labeled V_{gas}. If $h = 60$ mm Hg, what is the pressure exerted by the enclosed gas?



57. Velocity distribution curves are shown in the following graph for the same gas under two different conditions, A and B. Compare the behavior of the gas under conditions A and B in relation to each of the following:

a. temperature
b. average kinetic energy
c. average molecular velocity
d. gas volume
e. gas pressure



TECHNOLOGY & LEARNING

58. Graphing Calculator Deriving the Boyle's Law Equation

The graphing calculator can run a program that derives the equation for a curve, given data such as volume vs. pressure. Begin by creating a table of data. Then the program will plot the data.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

Note: Answers are written with two significant figures.

a. What is the pressure if the measured volume is 500 mL?
b. What is the volume if the measured pressure is 22 atm?
c. What is the volume if the measured pressure is 7.5 atm?

HANDBOOK SEARCH

59. Review the melting point data in the properties tables for each group of the *Elements Handbook*. What elements on the periodic table exist as gases at room temperature?

60. Review the listing found in the *Elements Handbook* of the top 10 chemicals produced in the United States. Which of the top 10 chemicals are gases?

61. Though mercury is an ideal liquid to use in barometers, it is highly toxic. Review the transition metals section of the *Elements Handbook*, and answer the following questions:

a. What is the density of mercury? How does the density of Hg compare with that of other transition metals?

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b. In what ways is mercury toxic?
c. What mercury compound is becoming more common as a pollutant in lakes and streams? Why is this pollutant so dangerous to freshwater ecosystems?
d. What are the symptoms of mercury poisoning?

RESEARCH & WRITING

62. Prepare a report on the development of the modern submarine. Include a discussion of the technology that enables the submarine to withstand the tremendous pressures at great ocean depths. Also report on the equipment used to ensure a sufficient supply of oxygen for submarine crew members.

63. Design and conduct a meteorological study to examine the interrelationships among barometric pressure, temperature, humidity, and other weather variables. Prepare a report explaining your results.

64. Conduct library research on attempts made to approach absolute zero and on the interesting properties that materials exhibit near that temperature. Write a report on your findings.

ALTERNATIVE ASSESSMENT

65. The air pressure of car tires should be checked regularly for safety reasons and to prevent uneven tire wear. Find out the units of measurement on a typical tire gauge, and determine how gauge pressure relates to atmospheric pressure.

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CHAPTER 11

Molecular Composition of Gases

The study of gases led to the formulation of the laws and principles that are the foundations of modern chemistry.

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Volume-Mass Relationships of Gases

SECTION 11-1

Objectives

- State the law of combining volumes.
- State Avogadro's law and explain its significance.
- Define *standard molar volume of a gas,* and use it to calculate gas masses and volumes.
- Use standard molar volume to calculate the molar mass of a gas.

In this section, you will study the relationships between the volumes of gases that react with each other. You will also learn how volume, density, and molar mass are related.

Measuring and Comparing the Volumes of Reacting Gases

In the early 1800s, French chemist Joseph Gay-Lussac studied gas volume relationships involving a chemical reaction between hydrogen and oxygen. He observed that 2 L of hydrogen can react with 1 L of oxygen to form 2 L of water vapor at constant temperature and pressure.

hydrogen gas	+	oxygen gas	⟶	water vapor
2 L		1 L		2 L
2 volumes		1 volume		2 volumes

In other words, this reaction shows a simple and definite 2:1:2 relationship between the volumes of the reactants and the product. Two volumes of hydrogen react with 1 volume of oxygen to produce 2 volumes of water vapor. The 2:1:2 relationship for this reaction applies to any proportions for volume—for example, 2 mL, 1 mL, and 2 mL; 600 L, 300 L, and 600 L; or 400 cm^3, 200 cm^3, and 400 cm^3.

Gay-Lussac also noticed simple and definite proportions by volume in other reactions of gases, such as in the reaction between hydrogen gas and chlorine gas.

hydrogen gas	+	chlorine gas	⟶	hydrogen chloride gas
1 L		1 L		2 L
1 volume		1 volume		2 volumes

In 1808, Gay-Lussac summarized the results of his experiments in a statement known today as **Gay-Lussac's law of combining volumes of gases.** The law states that *at constant temperature and pressure, the volumes of gaseous reactants and products can be expressed as ratios of small whole numbers.* This simple observation, combined with the insight of Avogadro, provided more understanding of how gases react and combine with each other.

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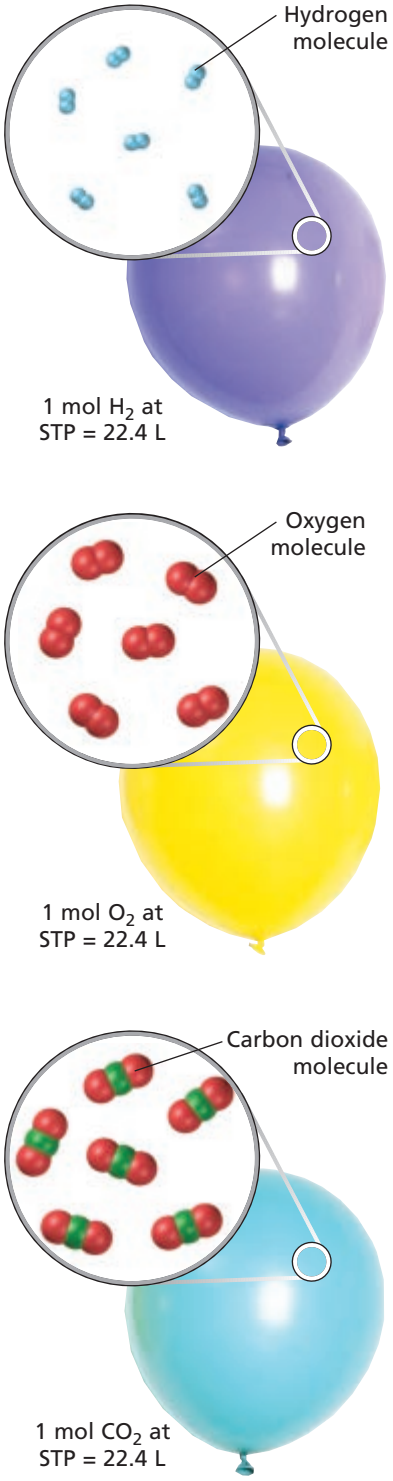

FIGURE 11-1 At the same temperature and pressure, balloons of equal volume have equal numbers of molecules, regardless of which gas they contain.

Avogadro's Law

Recall an important point of Dalton's atomic theory: atoms are indivisible. Dalton also thought that the particles of gaseous elements exist in the form of isolated single atoms. He believed that one atom of one element always combines with one atom of another element to form a single particle of the product. Accounting for some of the volume relationships observed by Gay-Lussac presented a problem for Dalton's theory. For example, in reactions such as the formation of water vapor, mentioned on the preceding page, it would seem that the oxygen involved would have to divide into two parts.

In 1811, Avogadro found a way to explain Gay-Lussac's simple ratios of combining volumes without violating Dalton's idea of indivisible atoms. He did this by rejecting Dalton's idea that reactant elements are always in monatomic form when they combine to form products. He reasoned that these molecules could contain more than one atom. Avogadro also put forth an idea known today as **Avogadro's law.** The law states that *equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.* Figure 11-1 illustrates Avogadro's law. It follows that at the same temperature and pressure, the volume of any given gas varies directly with the number of molecules.

Consider the reaction of hydrogen and chlorine to produce hydrogen chloride, illustrated in Figure 11-2. According to Avogadro's law, equal volumes of hydrogen and chlorine contain the same number of molecules. Avogadro accepted Dalton's idea that atoms of hydrogen and chlorine are indivisible. However, he rejected Dalton's belief that these elements are monatomic. He concluded that the hydrogen and chlorine components must each consist of two or more atoms joined together. The simplest assumption was that hydrogen and chlorine molecules are composed of two atoms each. That assumption leads to the following balanced equation for the reaction of hydrogen with chlorine.

$$\begin{array}{ccccc} H_2(g) & + & Cl_2(g) & \longrightarrow & 2HCl(g) \\ 1 \text{ volume} & & 1 \text{ volume} & & 2 \text{ volumes} \\ 1 \text{ molecule} & & 1 \text{ molecule} & & 2 \text{ molecules} \end{array}$$

The simplest hypothetical formula for hydrogen chloride, HCl, indicates that the molecule contains one hydrogen atom and one chlorine atom. Given the ratios of the combined volumes, the simplest formulas for hydrogen and chlorine must be H_2 and Cl_2, respectively.

Avogadro's reasoning applied equally well to the combining volumes for the reaction of hydrogen and oxygen to form water vapor. The simplest hypothetical formula for oxygen indicated two oxygen atoms, which turns out to be correct. The simplest possible molecule of water indicated two hydrogen atoms and one oxygen atom per molecule, which is also correct. Experiments eventually showed that all elements that are gases near room temperature, except the noble gases, normally exist as diatomic molecules.

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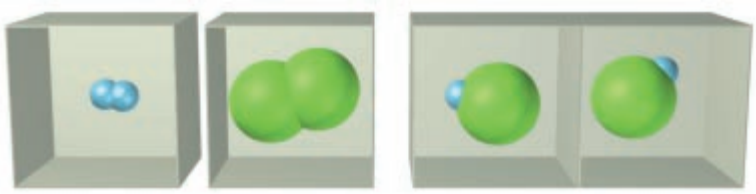

FIGURE 11-2 Hydrogen molecules combine with chlorine molecules in a 1:1 volume ratio to produce 2 volumes of hydrogen chloride.

Avogadro's law also indicates that gas volume is directly proportional to the amount of gas, at a given temperature and pressure. Note the equation for this relationship.

$$V = kn$$

Here, n is the amount of gas, in moles, and k is a constant. As shown below, the coefficients in a chemical reaction involving gases indicate the relative numbers of molecules, the relative numbers of moles, and the relative volumes.

$2H_2(g)$	+	$O_2(g)$	$\longrightarrow$	$2H_2O(g)$
2 molecules		1 molecule		2 molecules
2 mol		1 mol		2 mol
2 volumes		1 volume		2 volumes

Molar Volume of Gases

Recall that one mole of a molecular substance contains a number of molecules equal to Avogadro's constant (6.022×10^{23}). One mole of oxygen, O_2, contains 6.022×10^{23} diatomic oxygen molecules and has a mass of 31.9988 g. One mole of hydrogen contains the same number of diatomic hydrogen molecules but has a mass of only 2.015 88 g. One mole of helium, a monatomic gas, contains the same number of helium atoms and has a mass of 4.002 602 g.

According to Avogadro's law, one mole of any gas will occupy the same volume as one mole of any other gas at the same temperature and pressure, despite mass differences. *The volume occupied by one mole of a gas at STP is known as the* **standard molar volume of a gas.** *It has been found to be 22.414 10 L.* For calculations in this book, we use 22.4 L as the standard molar volume.

Knowing the volume of a gas, you can use 1 mol/22.4 L as a conversion factor to find the number of moles, and therefore the mass, of a given volume of a given gas at STP. You can also use the molar volume of a gas to find the volume, at STP, of a known number of moles or a known mass of a gas. These types of problems can also be solved using the ideal gas law, as you will see in Section 11-2.

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FIGURE 11-3 One-mole quantities of two different gases each occupy 22.4 L at STP and have equal numbers of molecules. However, their masses are different.

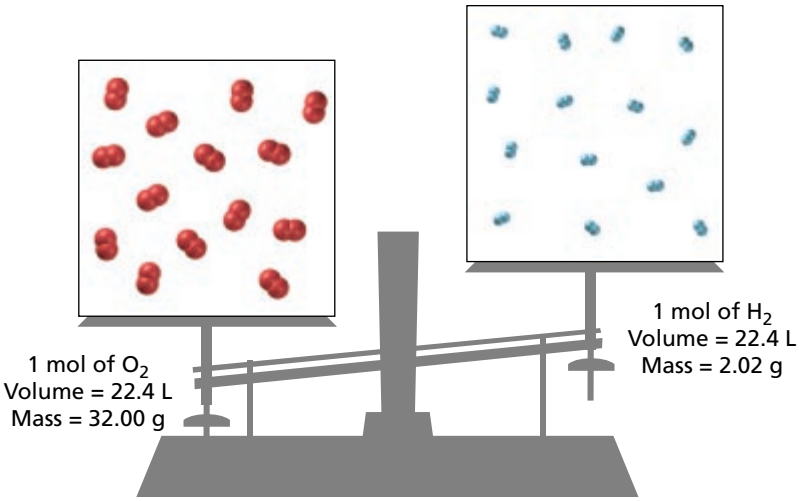

Figure 11-3 shows that 22.4 L of each gas contains the same number of molecules, but the mass of this volume is different for different gases. The mass of each is equal to the molar mass of the gas—the mass of one mole of molecules.

SAMPLE PROBLEM 11-1

A chemical reaction produces 0.0680 mol of oxygen gas. What volume in liters is occupied by this gas sample at STP?

SOLUTION

1 ANALYZE

Given: molar mass of O_2 = 0.0680 mol
Unknown: volume of O_2 in liters at STP

2 PLAN

$$\text{moles of } O_2 \longrightarrow \text{liters of } O_2 \text{ at STP}$$

The standard molar volume can be used to find the volume of a known molar amount of a gas at STP.

$$\text{mol} \times \frac{22.4\ \text{L}}{\text{mol}} = \text{volume of } O_2 \text{ in L}$$

3 COMPUTE

$$0.0680\ \cancel{\text{mol}}\ O_2 \times \frac{22.4\ \text{L}}{\cancel{\text{mol}}} = 1.52\ \text{L}\ O_2$$

4 EVALUATE

The answer is close to an estimated value of 1.4, computed as 0.07 × 20. Units have canceled to yield liters. The calculated result is correctly expressed to three significant figures.

PRACTICE

1. At STP, what is the volume of 7.08 mol of nitrogen gas?

Answer
159 L N_2

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2. A sample of hydrogen gas occupies 14.1 L at STP. How many moles of the gas are present?

Answer
0.629 mol H_2

3. At STP, a sample of neon gas occupies 550. cm^3. How many moles of neon gas does this represent?

Answer
0.0246 mol Ne

SAMPLE PROBLEM 11-2

A chemical reaction produced 98.0 mL of sulfur dioxide gas, SO_2, at STP. What was the mass (in grams) of the gas produced?

SOLUTION

1 ANALYZE

Given: volume of SO_2 at STP = 98.0 mL
Unknown: mass of SO_2 in grams

2 PLAN

$$\text{liters of } SO_2 \text{ at STP} \longrightarrow \text{moles of } SO_2 \longrightarrow \text{grams of } SO_2$$

$$\text{mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{1\text{ mol } SO_2}{22.4\text{ L}} \times \frac{\text{g } SO_2}{\text{mol } SO_2} = \text{g } SO_2$$

3 COMPUTE

$$98.0\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{1\ \cancel{\text{mol } SO_2}}{22.4\ \cancel{\text{L}}} \times \frac{64.07\text{ g } SO_2}{\cancel{\text{mol } SO_2}} = 0.280\text{ g } SO_2$$

4 EVALUATE

The result is correctly expressed to three significant figures. Units cancel correctly to give the answer in grams. The known volume is roughly 1/200 of the molar volume (22 400 mL/200 = 112 mL). The answer is reasonable: the mass should also be roughly 1/200 of the molar mass (64 g/200 = 0.32 g).

PRACTICE

1. What is the mass of 1.33×10^4 mL of oxygen gas at STP?

Answer
19.0 g O_2

2. What is the volume of 77.0 g of nitrogen dioxide gas at STP?

Answer
37.5 L NO_2

3. At STP, 3 L of chlorine is produced during a chemical reaction. What is the mass of this gas?

Answer
9 g Cl_2

SECTION REVIEW

1. Explain Gay-Lussac's law of combining volumes.
2. State Avogadro's law and explain its significance.
3. Define *molar volume.*
4. How many moles of oxygen gas are there in 135 L of oxygen at STP?
5. What volume (in mL) at STP will be occupied by 0.0035 mol of methane, CH_4?

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Chemistry's First Law

HISTORICAL PERSPECTIVE

The notion that nature abhors a vacuum was proposed by the Greek philosopher Aristotle, and his word went unchallenged for nearly 2000 years. Then in the mid-1600s, a new breed of thinkers known as experimental philosophers—later to be called scientists—began testing the long-held assumption that space must contain matter. These investigations represent some of the earliest experiments with gases, and they led to the discovery of the first empirical principle of chemistry, Boyle's law.

Overturning an Ancient Assumption

The first scientist to demonstrate the existence of a vacuum was Evangelista Torricelli. In 1643, he showed that when a glass tube 3 ft long and about an inch in diameter was sealed at one end, filled with mercury, and inverted in a container full of mercury, the mercury in the tube fell to a height of about 30 in. above the level of mercury in the container. Although some thinkers remained skeptical, it was generally accepted that the space between the mercury and the sealed end of the tube was indeed a vacuum.

Torricelli then turned his attention to how the mercury in the glass tube of his apparatus was supported. The known observation that liquids exerted a pressure on objects immersed in them inspired him to hypothesize that a "sea of air" surrounded Earth. He further hypothesized that the air exerted pressure on the mercury in the container and thus supported the mercury in the column.

Evangelista Torricelli invented the mercury barometer.

Support for the New Theory

Although the idea of an atmosphere that has weight and exerts a pressure on the objects within it seems obvious today, it was a radical theory at the time.

To test the effects of the atmosphere, one of the period's great scientists, Robert Boyle, had his talented assistant, Robert Hooke, create a piece of equipment that would revolutionize the study of air. The apparatus was an improved version of a pump designed by the famous German experimenter Otto von Guericke; the pump had a large receptacle in which a partial vacuum could be created.

Boyle placed Torricelli's setup, known today as a barometer, in the receptacle of the pump and observed the mercury column as he reduced the pressure around it. He noted that the height of the mercury decreased as the pressure surrounding the mercury in the container was lowered, strongly supporting Torricelli's atmospheric theory.

Using Hooke's pump, Boyle performed additional studies that verified the idea that air exerted pressure and had weight. His

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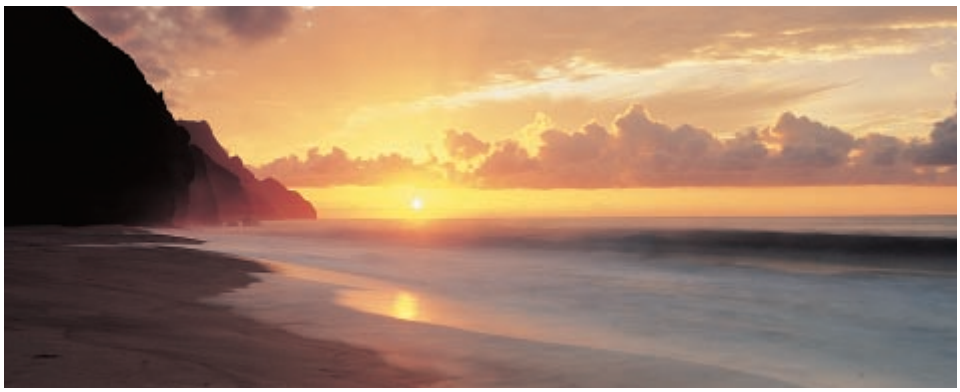
experiments also led him to the important conclusion that air was elastic, that is, it could expand and contract. It was during an investigation into air's elasticity that Boyle discovered the fundamental law that bears his name.



We can measure the difference between the atmospheric pressure on a mountaintop and the atmospheric pressure at sea level thanks to the work of Torricelli and Boyle.

An Ingenious Experiment

In response to a criticism of his findings, Boyle performed an experiment to show that air could be compressed to a pressure greater than that of the atmosphere. First he prepared a glass J tube with the short end sealed off and the long end left open. Then he poured mercury into the tube, making sure that the levels in each end were the same and letting air travel freely between the ends, to ensure that each column was at atmospheric pressure.

Boyle then poured more mercury into the long end of the tube until it was about 30 in. above the level of mercury in the short end, making the trapped air exposed to about twice as much atmospheric pressure. He observed that the volume of the trapped air was halved. He continued to add mercury until the total pressure on the trapped air was about four times that of the atmosphere.

Noting that the air had been compressed to about one-quarter of its original value, Boyle discovered the inverse relationship between air's pressure and its volume:

> *It is evident, that as common air, when reduced to half its wonted extent [volume], obtained near about twice as forcible a spring [pressure] as it had before; so this thus comprest air being further thrust into half this narrow room, obtained thereby a spring about . . . four times as strong as that of common air.*

A Long-Standing Contribution

Boyle went on to show that the relationship between air pressure and volume, $P \propto 1/V$ (at constant temperature), held not only when the gas was compressed but also when it was allowed to expand. It would be up to future investigators to show that the law was a principle applying to gases in general. Together with the findings of other researchers, such as Jacques Charles, Joseph Gay-Lussac, and Amadeo Avogadro, Boyle's discovery led chemists to the famous ideal gas law, $PV = nRT$, which serves as a starting point in the study of chemistry today.

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SECTION 11-2

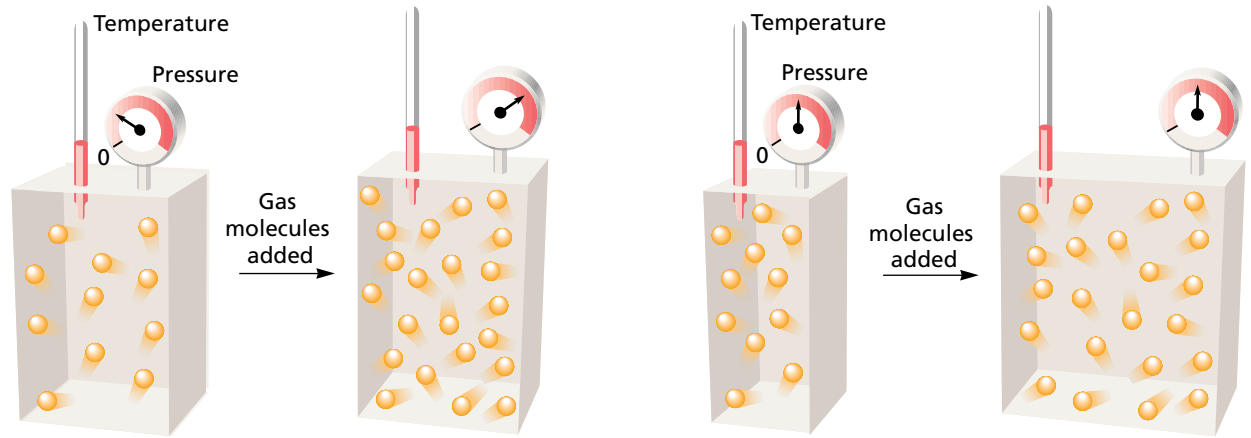
The Ideal Gas Law

Objectives

- State the ideal gas law.
- Derive the ideal gas constant and discuss its units.
- Using the ideal gas law, calculate pressure, volume, temperature, or amount of gas when the other three quantities are known.
- Using the ideal gas law, calculate the molar mass or density of a gas.
- Reduce the ideal gas law to Boyle's law, Charles's law, and Avogadro's law. Describe the conditions under which each applies.

In Section 10-3, you learned about three quantities—pressure, volume, and temperature—needed to describe a gas sample. A gas sample can be further characterized using a fourth quantity—the number of moles. The number of molecules or moles present will always affect at least one of the other three quantities. The collision rate of molecules per unit area of container wall depends on the number of molecules present. If the number of molecules is increased for a sample at constant volume and temperature, the collision rate increases. Therefore, the pressure increases, as shown by the model in Figure 11-4(a). Consider what would happen if the pressure and temperature were kept constant while the number of molecules increased. According to Avogadro's law, the volume would increase. As Figure 11-4(b) shows, an increase in volume keeps the pressure constant at constant temperature. Increasing the volume keeps the collision rate per unit of wall area constant.

You can see that gas pressure, volume, temperature, and the number of moles are all interrelated. There is a mathematical relationship that describes the behavior of a gas sample for any combination of these conditions. *The* **ideal gas law** *is the mathematical relationship among pressure, volume, temperature, and the number of moles of a gas.* It is the equation of state for an ideal gas, because the state of a gas can be defined by its pressure, volume, temperature, and number of moles.



(a) (b)

FIGURE 11-4 (a) When volume and temperature are constant, gas pressure increases as the number of molecules increases. (b) When pressure and temperature are constant, gas volume increases as the number of molecules increases.

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Derivation of the Ideal Gas Law

The general equation that can be used to calculate unknown information about gas samples can be derived by combining Boyle's law and Charles's law with a statement that follows logically from Avogadro's law. First, consider each of those laws and the principle again.

Boyle's law: At constant temperature, the volume of a given mass of gas is inversely proportional to the pressure.

$$V \propto \frac{1}{P}$$

Charles's law: At constant pressure, the volume of a given mass of gas is directly proportional to the Kelvin temperature.

$$V \propto T$$

Avogadro's law implies that at constant pressure and temperature, the volume of a given mass of a gas is directly proportional to the number of moles.

$$V \propto n$$

A quantity—in this case, volume—that is proportional to each of several quantities is also proportional to their product. Therefore, combining the three relationships above gives the following.

$$V \propto \frac{1}{P} \times T \times n$$

Mathematically, you can change a proportionality to an equality by introducing a constant. In this case, the symbol R is used for the constant.

$$V = R \times \frac{1}{P} \times T \times n$$

R represents the value that the quantity PV/nT approaches for any gas whose behavior approaches that of an ideal gas. The equation for the ideal gas law is derived as follows.

$$V = \frac{nRT}{P} \text{ or } PV = nRT$$

This equation states that the volume of a gas varies directly with the number of moles (or molecules) of a gas and its Kelvin temperature. The volume also varies inversely with the pressure. Under ordinary conditions, most gases exhibit behavior that is nearly ideal. The equation can then be applied with reasonable accuracy.

The ideal gas law reduces to Boyle's law, Charles's law, Gay-Lussac's law, or Avogadro's law when the appropriate variables are held constant. For example, if n and T are constant, the product nRT is constant because R is also constant. In this case, the ideal gas law reduces to PV = a constant, which is Boyle's law.

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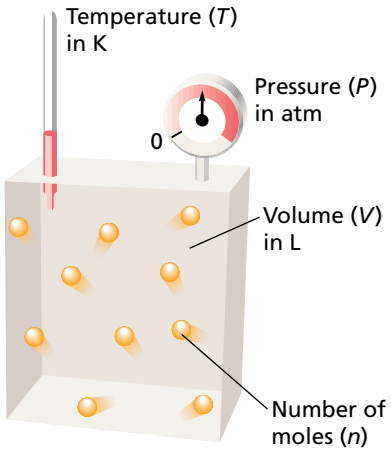

FIGURE 11-5 The ideal gas law relates the pressure, volume, number of moles, and temperature of an ideal gas. Note the value of the gas constant, *R*, when the other quantities are in the units shown.

The Ideal Gas Constant

In the equation representing the ideal gas law, *the constant R is known as the* **ideal gas constant.** Its value depends on the units chosen for pressure, volume, and temperature. Figure 11-5 shows that measured values of *P, V, T,* and *n* for a gas at near-ideal conditions can be used to calculate *R*. Recall from Section 11-1 that the volume of one mole of an ideal gas at STP (1 atm and 273.15 K) is 22.414 10 L. Substituting these values and solving the ideal gas law equation for *R* gives the following.

$$R = \frac{PV}{nT} = \frac{(1\text{ atm})(22.414\ 10\text{ L})}{(1\text{ mol})(273.15\text{ K})} = 0.082\ 057\ 84\ \frac{\text{L•atm}}{\text{mol•K}}$$

This calculated value of *R* is usually rounded to 0.0821 L•atm/(mol•K). Use this value in ideal gas law calculations when the volume is in liters, the pressure is in atmospheres, and the temperature is in kelvins. See Table 11-1 for the value of *R* when other units for *n, P, V,* and *T* are used.

Finding *P, V, T,* or *n* from the Ideal Gas Law

The ideal gas law can be applied to determine the existing conditions of a gas sample when three of the four variables, *P, V, T,* and *n,* are known. It can also be used to calculate the molar mass or density of a gas sample.

Be sure to match the units of the known quantities and the units of *R*. In this book, you will be using *R* = 0.0821 L•atm/(mol•K). Your first step in solving any ideal gas law problem should be to check the known values to be sure you are working with the correct units. If necessary, you must convert volumes to liters, pressures to atmospheres, temperatures to kelvins, and masses to numbers of moles before using the ideal gas law.

TABLE 11-1 *Numerical Values of the Gas Constant, R*

Unit of *R*	Numerical value of *R*	Unit of *P*	Unit of *V*	Unit of *T*	Unit of *n*
$\frac{\text{L•mm Hg}}{\text{mol•K}}$	62.4	mm Hg	L	K	mol
$\frac{\text{L•atm}}{\text{mol•K}}$	0.0821	atm	L	K	mol
$\frac{\text{J}}{\text{mol•K}}$	8.314*	Pa	m^3	K	mol
$\frac{\text{L•kPa}}{\text{mol•K}}$	8.314	kPa	L	K	mol

Note: 1 L•atm = 101.325 J; 1 J = 1 Pa•m^3
* SI units

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SAMPLE PROBLEM 11-3

What is the pressure in atmospheres exerted by a 0.500 mol sample of nitrogen gas in a 10.0 L container at 298 K?

SOLUTION

1 ANALYZE

Given: V of $N_2 = 10.0$ L
n of $N_2 = 0.500$ mol
T of $N_2 = 298$ K

Unknown: P of N_2 in atm

2 PLAN

$$n, V, T \longrightarrow P$$

The gas sample undergoes no change in conditions. Therefore, the ideal gas law can be rearranged and used to find the pressure as follows.

$$P = \frac{nRT}{V}$$

3 COMPUTE

$$P = \frac{(0.500\ \text{mol})\left(\frac{0.0821\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298\ \text{K})}{10.0\ \text{L}} = 1.22\ \text{atm}$$

4 EVALUATE

All units cancel correctly to give the result in atmospheres. The answer is properly limited to three significant figures. It is also close to an estimated value of 1.5, computed as $(0.5 \times 0.1 \times 300)/10$.

PRACTICE

1. What pressure, in atmospheres, is exerted by 0.325 mol of hydrogen gas in a 4.08 L container at 35°C? *Answer* 2.01 atm
2. A gas sample occupies 8.77 L at 20°C. What is the pressure, in atmospheres, given that there are 1.45 mol of gas in the sample? *Answer* 3.98 atm

SAMPLE PROBLEM 11-4

What is the volume, in liters, of 0.250 mol of oxygen gas at 20.0°C and 0.974 atm pressure?

SOLUTION

1 ANALYZE

Given: P of $O_2 = 0.974$ atm
n of $O_2 = 0.250$ mol
To use the value 0.0821 L•atm/(mol•K) for R, the temperature (°C) must be converted to kelvins.
T of $O_2 = 20.0°C + 273.2 = 293.2$ K

Unknown: V of O_2 in L

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2 PLAN

$$P, n, T \longrightarrow V$$

The ideal gas law can be rearranged to solve for V for this sample, which undergoes no change in conditions.

$$V = \frac{nRT}{P}$$

3 COMPUTE

$$V = \frac{(0.250 \text{ mol } O_2)\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(293.2 \text{ K})}{0.974 \text{ atm}} = 6.17 \text{ L } O_2$$

4 EVALUATE

Units cancel to give liters, as desired. The answer is correctly limited to three significant figures. It is also close to an estimated value of 6, calculated as $0.2 \times 0.1 \times 300$.

PRACTICE

1. A sample that contains 4.38 mol of a gas at 250 K has a pressure of 0.857 atm. What is the volume? *Answer* 105 L

2. How many liters are occupied by 0.909 mol of nitrogen at 125°C and 0.901 atm pressure? *Answer* 33.0 L N_2

SAMPLE PROBLEM 11-5

What mass of chlorine gas, Cl_2, in grams, is contained in a 10.0 L tank at 27°C and 3.50 atm of pressure?

SOLUTION

1 ANALYZE

Given: P of $Cl_2 = 3.50$ atm
V of $Cl_2 = 10.0$ L
T of $Cl_2 = 27°C + 273 = 300.$ K

Unknown: mass of Cl_2 in g

2 PLAN

The ideal gas law can be rearranged to solve for n after temperature is converted to kelvins.

$$n = \frac{PV}{RT}$$

The number of moles is then converted to grams.

$$m \text{ (in g)} = n \times \frac{\text{g}}{\text{mol}}$$

3 COMPUTE

$$n = \frac{(3.50 \text{ atm})(10.0 \text{ L } Cl_2)}{\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(300. \text{ K})} = 1.42 \text{ mol } Cl_2$$

$$\text{mass of } Cl_2 = 1.42 \text{ mol} \times \frac{70.90 \text{ g } Cl_2}{\text{mol}} = 101 \text{ g } Cl_2$$

4 EVALUATE

Units cancel to leave the desired unit. The result is correctly given to three significant figures. The answer is close to the estimated value.

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PRACTICE

1. How many grams of carbon dioxide gas are there in a 45.1 L container at 34°C and 1.04 atm? *Answer* 81.9 g CO_2
2. What is the mass, in grams, of oxygen gas in a 12.5 L container at 45°C and 7.22 atm? *Answer* 111 g O_2
3. A sample of carbon dioxide with a mass of 0.30 g was placed in a 250 mL container at 400. K. What is the pressure exerted by the gas? *Answer* 0.90 atm

Finding Molar Mass or Density from the Ideal Gas Law

Suppose that the pressure, volume, temperature, and mass are known for a gas sample. You can calculate the number of moles (n) in the sample, using the ideal gas law. Then you can calculate the molar mass (grams per mole) by dividing the known mass by the number of moles.

An equation showing the relationship between density, pressure, temperature, and molar mass can be derived from the ideal gas law. The number of moles (n) is equal to mass (m) divided by molar mass (M). Substituting m/M for n into $PV = nRT$ gives the following.

$$PV = \frac{mRT}{M} \text{ or } M = \frac{mRT}{PV}$$

Density (D) is mass (m) per unit volume (V). Writing this definition in the form of an equation gives $D = m/V$. You can see that m/V appears in the right-hand equation above. Introducing density into that equation gives the following.

$$M = \frac{mRT}{PV} = \frac{DRT}{P}$$

Solving for density gives this equation.

$$D = \frac{MP}{RT}$$

You can see that the density of a gas varies directly with molar mass and pressure and inversely with Kelvin temperature.

SAMPLE PROBLEM 11-6

At 28°C and 0.974 atm, 1.00 L of gas has a mass of 5.16 g. What is the molar mass of this gas?

SOLUTION

1 ***ANALYZE***

Given: P of gas = 0.974 atm
V of gas = 1.00 L
T of gas = 28°C + 273 = 301 K
m of gas = 5.16 g

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Unknown: M of gas in g/mol

2 PLAN

$$P, V, T, m \longrightarrow M$$

You can use the rearranged ideal gas law provided earlier in this section to find the answer.

$$M = \frac{mRT}{PV}$$

3 COMPUTE

$$M = \frac{(5.16\text{ g})\left(\frac{0.0821\ \cancel{\text{L}} \cdot \cancel{\text{atm}}}{\text{mol} \cdot \cancel{\text{K}}}\right)(301\ \cancel{\text{K}})}{(0.974\ \cancel{\text{atm}})(1.00\ \cancel{\text{L}})} = 131\text{ g/mol}$$

4 EVALUATE

Units cancel as needed. The answer is correctly given to three significant figures. It is also close to an estimated value of 150, calculated as $(5 \times 0.1 \times 300)/1$.

PRACTICE

1. What is the molar mass of a gas if 0.427 g of the gas occupies a volume of 125 mL at 20.0°C and 0.980 atm?
   Answer 83.8 g/mol
2. What is the density of a sample of ammonia gas, NH_3, if the pressure is 0.928 atm and the temperature is 63.0°C?
   Answer 0.572 g/L NH_3
3. The density of a gas was found to be 2.0 g/L at 1.50 atm and 27°C. What is the molar mass of the gas?
   Answer 33 g/mol
4. What is the density of argon gas, Ar, at a pressure of 551 torr and a temperature of 25°C?
   Answer 1.18 g/L Ar

SECTION REVIEW

1. How does the ideal gas law reduce to the following:
   a. Boyle's law
   b. Charles's law
   c. Gay-Lussac's law
   d. Avogadro's law
2. What is the volume, in liters, of 0.100 g of $C_2H_2F_4$ vapor at 0.0928 atm and 22.3°C?
3. Why must the units P, V, T, and n match up to those of the ideal gas constant in solving problems? What would be the units for R if P is in pascals, T is in kelvins, V is in liters, and n is in moles?
4. What is the molar mass of a 1.25 g sample of gas that occupies a volume of 1.00 L at a pressure of 0.961 atm and a temperature of 27.0°C?
5. Name two quantities besides pressure, mass, volume, and number of moles that can be calculated using the ideal gas law.

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Stoichiometry of Gases

SECTION 11-3

Objectives

- Explain how Gay-Lussac's law and Avogadro's law apply to the volumes of gases in chemical reactions.
- Use a chemical equation to specify volume ratios for gaseous reactants or products, or both.
- Use volume ratios and the gas laws to calculate volumes, masses, or molar amounts of gaseous reactants or products.

You can apply the discoveries of Gay-Lussac and Avogadro to calculate the stoichiometry of reactions involving gases. For gaseous reactants or products, the coefficients in chemical equations not only indicate molar amounts and mole ratios but also reveal volume ratios. For example, consider the reaction of carbon monoxide with oxygen to give carbon dioxide.

$$\begin{array}{ccccc} 2CO(g) & + & O_2(g) & \longrightarrow & 2CO_2(g) \\ 2 \text{ molecules} & & 1 \text{ molecule} & & 2 \text{ molecules} \\ 2 \text{ mol} & & 1 \text{ mol} & & 2 \text{ mol} \\ 2 \text{ volumes} & & 1 \text{ volume} & & 2 \text{ volumes} \end{array}$$

The possible volume ratios can be expressed in the following ways.

a. $\dfrac{2 \text{ volumes CO}}{1 \text{ volume } O_2}$ or $\dfrac{1 \text{ volume } O_2}{2 \text{ volumes CO}}$

b. $\dfrac{2 \text{ volumes CO}}{2 \text{ volumes } CO_2}$ or $\dfrac{2 \text{ volumes } CO_2}{2 \text{ volumes CO}}$

c. $\dfrac{1 \text{ volume } O_2}{2 \text{ volumes } CO_2}$ or $\dfrac{2 \text{ volumes } CO_2}{1 \text{ volume } O_2}$

Volumes can be compared in this way only if all are measured at the same temperature and pressure.

Volume-Volume Calculations

Suppose the volume of a gas involved in a reaction is known and you need to find the volume of another gaseous reactant or product, assuming both reactant and product exist under the same conditions. Use volume ratios like those given above in exactly the same way you would use mole ratios.

SAMPLE PROBLEM 11-7

Propane, C_3H_8, is a gas that is sometimes used as a fuel for cooking and heating. The complete combustion of propane occurs according to the following equation.

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

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(a) What will be the volume, in liters, of oxygen required for the complete combustion of 0.350 L of propane? (b) What will be the volume of carbon dioxide produced in the reaction? Assume that all volume measurements are made at the same temperature and pressure.

SOLUTION

1 ANALYZE

Given: balanced chemical equation
V of propane = 0.350 L

Unknown: **a.** V of O_2 in L; **b.** V of CO_2 in L

2 PLAN

a. V of $C_3H_8 \longrightarrow V$ of O_2; **b.** V of $C_3H_8 \longrightarrow V$ of CO_2

All volumes are to be compared at the same temperature and pressure. Therefore, volume ratios can be used like mole ratios to find the unknowns.

3 COMPUTE

$$\textbf{a. } 0.350 \cancel{\text{ L } C_3H_8} \times \frac{5 \text{ L } O_2}{1 \cancel{\text{ L } C_3H_8}} = 1.75 \text{ L } O_2$$

$$\textbf{b. } 0.350 \cancel{\text{ L } C_3H_8} \times \frac{3 \text{ L } CO_2}{1 \cancel{\text{ L } C_3H_8}} = 1.05 \text{ L } CO_2$$

4 EVALUATE

Each result is correctly given to three significant figures. The answers are reasonably close to estimated values of 2, calculated as 0.4×5, and 1.2, calculated as 0.4×3, respectively.

PRACTICE

1. Assuming all volume measurements are made at the same temperature and pressure, what volume of hydrogen gas is needed to react completely with 4.55 L of oxygen gas to produce water vapor?

   Answer 9.10 L H_2

2. What volume of oxygen gas is needed to react completely with 0.626 L of carbon monoxide gas, CO, to form gaseous carbon dioxide? Assume all volume measurements are made at the same temperature and pressure.

   Answer 0.313 L O_2

CHEMISTRY INTERACTIVE TUTOR

Module 5: Equations and Stoichiometry

Volume-Mass and Mass-Volume Calculations

Stoichiometric calculations may involve both masses and gas volumes. Sometimes the volume of a reactant or product is given and the mass of a second gaseous substance is unknown. In other cases, a mass amount may be known and a volume may be the unknown. The calculations require routes such as the following.

gas volume A $\longrightarrow$ moles A $\longrightarrow$ moles B $\longrightarrow$ mass B

or

mass A $\longrightarrow$ moles A $\longrightarrow$ moles B $\longrightarrow$ gas volume B

To find the unknown in cases like these, you must know the conditions under which both the known and unknown gas volumes have been measured. The ideal gas law is useful for calculating values at standard and nonstandard conditions.

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SAMPLE PROBLEM 11-8

Calcium carbonate, $CaCO_3$, also known as limestone, can be heated to produce calcium oxide (lime), an industrial chemical with a wide variety of uses. The balanced equation for the reaction follows.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

How many grams of calcium carbonate must be decomposed to produce 5.00 L of carbon dioxide gas at STP?

SOLUTION

1 ANALYZE

Given: balanced chemical equation
desired volume of CO_2 produced at STP = 5.00 L

Unknown: mass of $CaCO_3$ in grams

2 PLAN

The known volume is given at STP. This tells us the pressure and temperature. The ideal gas law can be used to find the moles of CO_2. The mole ratios from the balanced equation can then be used to calculate the moles of $CaCO_3$ needed. (Note that volume ratios do not apply here because calcium carbonate is a solid.)

3 COMPUTE

$$n = \frac{PV}{RT} = \frac{(1\ \cancel{atm})(5.00\ \cancel{L}\ CO_2)}{\left(\frac{0.0821\ \cancel{L} \cdot \cancel{atm}}{mol \cdot \cancel{K}}\right)(273\ \cancel{K})} = 0.223\ mol\ CO_2$$

$$0.223\ \cancel{mol\ CO_2} \times \frac{1\ \cancel{mol\ CaCO_3}}{1\ \cancel{mol\ CO_2}} \times \frac{100.09\ g\ CaCO_3}{1\ \cancel{mol\ CaCO_3}} = 22.3\ g\ CaCO_3$$

4 EVALUATE

Units all cancel correctly. The answer is properly given to three significant figures. It is close to an estimated value of 20, computed as $(0.2 \times 100)/25$.

PRACTICE

1. What mass of sulfur must be used to produce 12.61 L of gaseous sulfur dioxide at STP according to the following equation? *Answer* 18.0 g S_8

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$

2. How many grams of water can be produced from the complete reaction of 3.44 L of oxygen gas, at STP, with hydrogen gas? *Answer* 5.53 g H_2O

SAMPLE PROBLEM 11-9

Tungsten, W, a metal used in light-bulb filaments, is produced industrially by the reaction of tungsten oxide with hydrogen.

$$WO_3(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(l)$$

How many liters of hydrogen gas at 35°C and 0.980 atm are needed to react completely with 875 g of tungsten oxide?

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SOLUTION

1 ANALYZE

Given: balanced chemical equation
reactant mass of $WO_3 = 875$ g
P of $H_2 = 0.980$ atm
T of $H_2 = 35°C + 273 = 308$ K

Unknown: V of H_2 in L at known nonstandard conditions

2 PLAN

Moles of H_2 are found by converting the mass of WO_3 to moles and then using the mole ratio. The ideal gas law is used to find the volume from the calculated number of moles of H_2.

3 COMPUTE

$$875 \text{ g } \cancel{WO_3} \times \frac{1 \text{ } \cancel{\text{mol } WO_3}}{231.84 \text{ } \cancel{\text{g } WO_3}} \times \frac{3 \text{ mol } H_2}{1 \text{ } \cancel{\text{mol } WO_3}} = 11.3 \text{ mol } H_2$$

$$V = \frac{nRT}{P} = \frac{(11.3 \text{ } \cancel{\text{mol}} \text{ } H_2)\left(\frac{0.0821 \text{ L} \cdot \cancel{\text{atm}}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}}\right)(308 \text{ } \cancel{\text{K}})}{0.980 \text{ } \cancel{\text{atm}}} = 292 \text{ L } H_2$$

4 EVALUATE

Unit cancellations are correct, as is the use of three significant figures for each result. The answer is reasonably close to an estimated value of 330, computed as $(11 \times 0.1 \times 300)/1$.

PRACTICE

1. What volume of chlorine gas at 38°C and 1.63 atm is needed to react completely with 10.4 g of sodium to form NaCl?

   Answer
   3.54 L Cl_2

2. How many liters of gaseous carbon monoxide at 27°C and 0.247 atm can be produced from the burning of 65.5 g of carbon according to the following equation?

   $$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

   Answer
   544 L CO

SECTION REVIEW

1. How many liters of ammonia gas can be formed from the reaction of 150. L of hydrogen gas? Assume that there is complete reaction of hydrogen with excess nitrogen gas and that all measurements are made at the same temperature and pressure.
2. How many liters of H_2 gas at STP can be produced by the reaction of 4.60 g of Na and excess water, according to the following equation?

   $$2Na(s) + 2H_2O(l) \longrightarrow H_2(g) + 2NaOH(aq)$$

3. How many grams of Na are needed to react with H_2O to liberate 4.00×10^2 mL of H_2 gas at STP?
4. What volume of oxygen gas in liters can be collected at 0.987 atm pressure and 25.0°C when 30.6 g of $KClO_3$ decompose by heating, according to the following equation?

   $$2KClO_3(s) \xrightarrow[MnO_2]{\Delta} 2KCl(s) + 3O_2(g)$$

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Effusion and Diffusion

SECTION 11-4

Objectives

- State Graham's law of effusion.
- Determine the relative rates of effusion of two gases of known molar masses.
- State the relationship between the molecular velocities of two gases and their molar masses.

The constant motion of gas molecules causes them to spread out to fill any container in which they are placed. As you learned in Chapter 10, the gradual mixing of two gases due to their spontaneous, random motion is known as *diffusion,* illustrated in Figure 11-6. *Effusion* is the process whereby the molecules of a gas confined in a container randomly pass through a tiny opening in the container. In this section, you will learn how effusion can be used to estimate the molar mass of a gas.

Graham's Law of Effusion

The rates of effusion and diffusion depend on the relative velocities of gas molecules. The velocity of a gas varies inversely with its mass. Lighter molecules move faster than heavier molecules at the same temperature.

Recall that the average kinetic energy of the molecules in any gas depends only on the temperature and equals $\frac{1}{2}mv^2$. For two different gases, A and B, at the same temperature, the following relationship is true.

$$\frac{1}{2}M_A{v_A}^2 = \frac{1}{2}M_B{v_B}^2$$

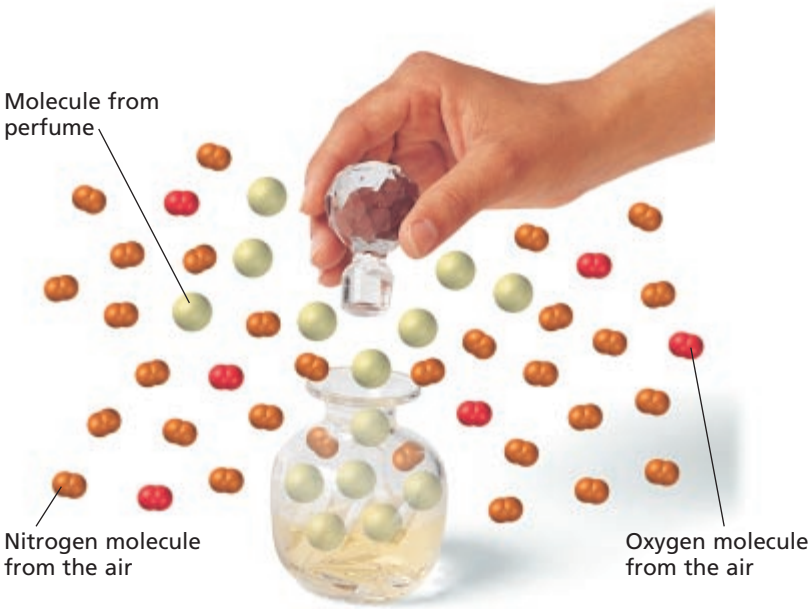

FIGURE 11-6 When a bottle of perfume is opened, some of its molecules diffuse into the air and mix with the molecules in the air. At the same time, molecules from the air, such as nitrogen and oxygen, diffuse into the bottle and mix with the gaseous scent molecules.

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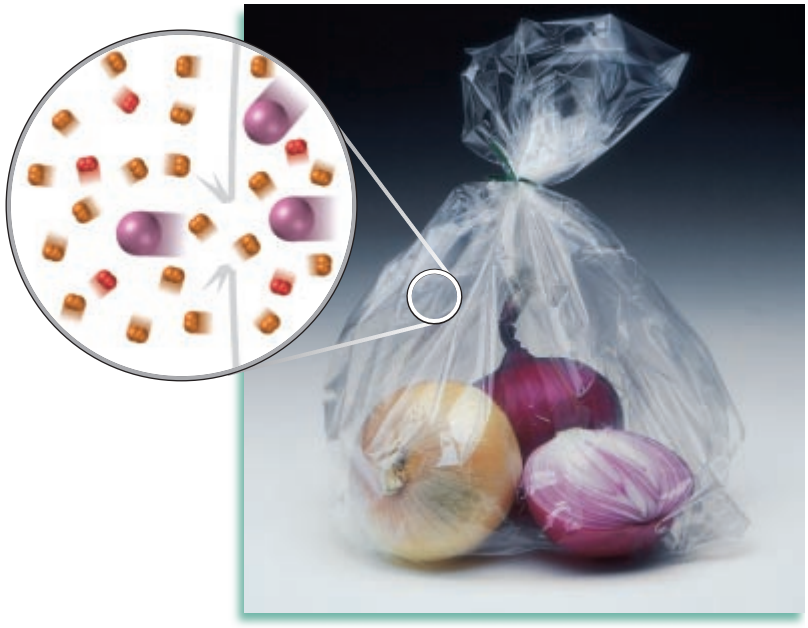

FIGURE 11-7 If you can smell the onions even when the bag is tightly sealed, molecules from the onions may be effusing through a small hole in the bag.

M_A and M_B represent the molar masses of gases A and B, and v_A and v_B represent their molecular velocities. Multiplying the equation by 2 gives the following.

$$M_A v_A^2 = M_B v_B^2$$

Suppose you wanted to compare the velocities of the two gases. You would first rearrange the equation above to give the velocities as a ratio.

$$\frac{v_A^2}{v_B^2} = \frac{M_B}{M_A}$$

The square root of each side of the equation is then taken.

$$\frac{v_A}{v_B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

This equation shows that the molecular velocities of two different gases are inversely proportional to the square roots of their molar masses. Because the rates of effusion are directly proportional to molecular velocities, the equation can be written as follows.

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

In the mid-1800s, the Scottish chemist Thomas Graham studied the effusion and diffusion of gases. Figure 11-7 illustrates the process of effusion. Compare this with the diffusion process. The equation derived above is a mathematical statement of some of Graham's discoveries. It describes the rates of effusion. **Graham's law of effusion** *states that the rates of effusion of gases at the same temperature and pressure are inversely proportional to the square roots of their molar masses.*

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Quick LAB

Diffusion

Wear Safety Goggles and an Apron.

Materials

- household ammonia
- perfume or cologne
- two 250 mL beakers
- Two watch glasses
- 10 mL graduated cylinder
- clock or watch with second hand

Question

Do different gases diffuse at different rates?

Procedure

Record all of your results in a data table.

1. Outdoors or in a room separate from the one in which you will carry out the rest of the investigation, pour approximately 10 mL of the household ammonia into one of the 250 mL beakers, and cover it with a watch glass. Pour roughly the same amount of perfume or cologne into the second beaker. Cover it with a watch glass also.

2. Take the two samples you just prepared into a large, draft-free room. Place the samples about 12 to 15 feet apart and at the same height. Position someone as the observer midway between the two beakers. Remove both watch-glass covers at the same time.
3. Note whether the observer smells the ammonia or the perfume first. Record how long this takes. Also, record how long it takes the vapor of the other substance to reach them. Air the room after you have finished.

Discussion

1. What do the times that the two vapors took to reach the observer show about the two gases?
2. What factors other than molecular mass (which determines diffusion rate) could affect how quickly the observer smells each vapor?

Applications of Graham's Law

Graham's experiments dealt with the densities of gases. The density of a gas varies directly with its molar mass. Therefore, the square roots of the molar masses in the equation on page 352 can be replaced by the square roots of the gas densities, giving the following relationship.

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}} = \frac{\sqrt{\text{density}_B}}{\sqrt{\text{density}_A}}$$

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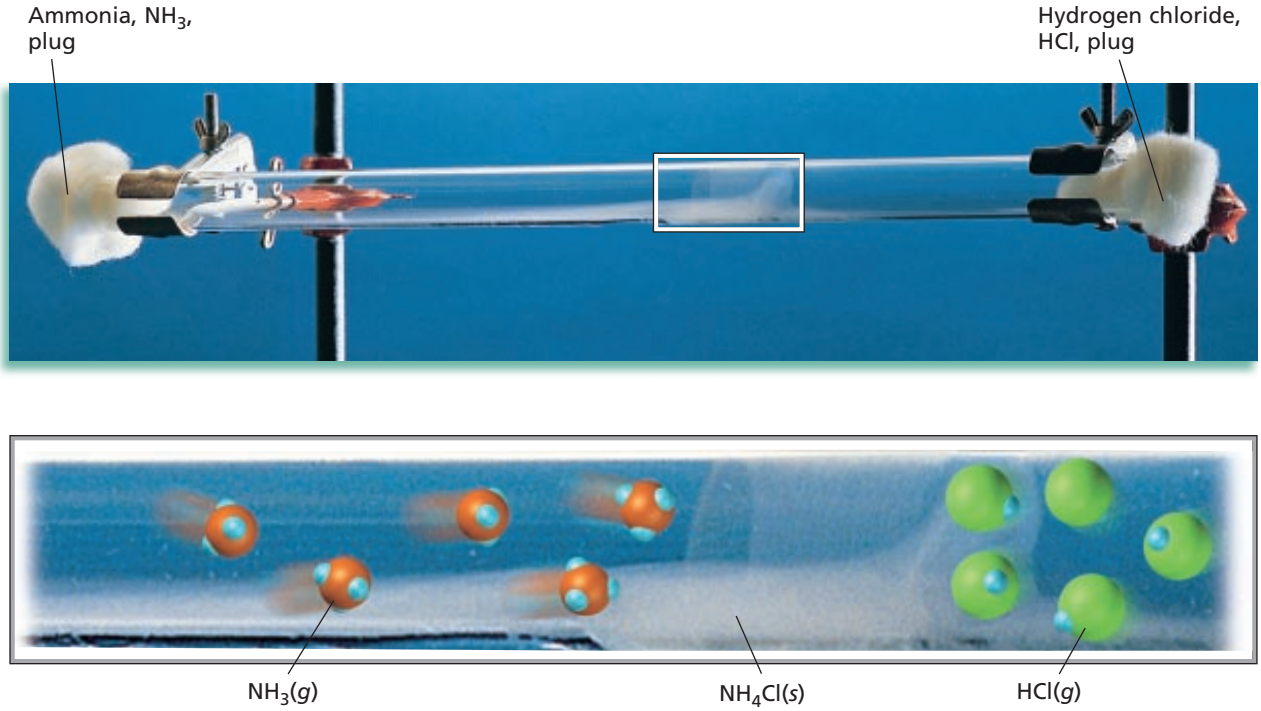
In the experiment shown in Figure 11-8, ammonia gas, NH_3, and hydrogen chloride gas, HCl, diffuse toward each other from opposite ends of a glass tube. A white ring forms at the point where the two gases meet and combine chemically. The white ring is solid ammonium chloride, NH_4Cl. Notice that it forms closer to the HCl end of the tube than to the NH_3 end. The NH_3 has diffused faster than the HCl.

If the two gases had equal vapor pressures (resulting in equal concentrations), this result could be attributed completely to differences in molar mass. The lighter NH_3 molecules (molar mass 17.04 g) diffuse faster than the heavier HCl molecules (molar mass 36.46 g). However, diffusion rates depend on both molar mass and concentration.

The diffusion of the two gases in the tube takes longer than would be predicted from the known velocities of NH_3 and HCl. This is because the experiment does not take place in a vacuum. The oxygen and nitrogen molecules present in the air collide with the diffusing ammonia and hydrogen chloride molecules, slowing them down. To describe all these random collisions taking place in this system would be very complicated. This is why we use these equations to represent the *relative* rates of effusion based on the *relative* velocities of the molecules.

Graham's law also provides a method for determining molar masses. The rates of effusion of gases of known and unknown molar mass can be compared at the same temperature and pressure. The unknown molar mass can then be calculated using Graham's law. One application of Graham's law was used in order to separate the heavier $^{238}_{92}U$ isotope from the lighter $^{235}_{92}U$ isotope. The uranium was converted to a gaseous compound and passed through porous membranes, where the isotopes diffused at different rates due to their different densities and were thereby separated.

FIGURE 11-8 Cotton plugs moistened with solutions of ammonia and hydrogen chloride were placed at opposite ends of the glass tube several minutes before this photograph was taken. Why does the white ring of ammonium chloride form closer to the right end than the left end?



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SAMPLE PROBLEM 11-10

Compare the rates of effusion of hydrogen and oxygen at the same temperature and pressure.

SOLUTION

1 ANALYZE

Given: identities of two gases, H_2 and O_2
Unknown: relative rates of effusion

2 PLAN

molar mass ratio $\longrightarrow$ ratio of rates of effusion

The ratio of the rates of effusion of two gases at the same temperature and pressure can be found from Graham's law.

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

3 COMPUTE

$$\frac{\text{rate of effusion of } H_2}{\text{rate of effusion of } O_2} = \frac{\sqrt{M_{O_2}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{32.00\ \text{g/mol}}}{\sqrt{2.02\ \text{g/mol}}} = \sqrt{\frac{32.00\ \text{g/mol}}{2.02\ \text{g/mol}}} = 3.98$$

Hydrogen effuses 3.98 times faster than oxygen.

4 EVALUATE

The result is correctly reported to three significant figures. It is also approximately equivalent to an estimated value of 4, calculated as $\sqrt{32}\,/\sqrt{2}$.

PRACTICE

1. A sample of hydrogen effuses through a porous container about 9 times faster than an unknown gas. Estimate the molar mass of the unknown gas.

   Answer
   160 g/mol

2. Compare the rate of effusion of carbon dioxide with that of hydrogen chloride at the same temperature and pressure.

   Answer
   CO_2 will effuse about 0.9 times as fast as HCl.

3. If a molecule of neon gas travels at an average of 400 m/s at a given temperature, estimate the average speed of a molecule of butane gas, C_4H_{10}, at the same temperature.

   Answer
   about 235 m/s

SECTION REVIEW

1. Compare diffusion with effusion.
2. Estimate the molar mass of a gas that effuses at 1.6 times the effusion rate of carbon dioxide.
3. List the following gases in order of increasing average molecular velocity at 25°C: H_2O, He, HCl, BrF, and NO_2.

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CHAPTER 11 REVIEW

CHAPTER SUMMARY

11-1

- Gay-Lussac's law of combining volumes of gases states that the volumes of reacting gases and their products at the same temperature and pressure can be expressed as ratios of small whole numbers.
- Avogadro's law states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. At constant temperature and pressure, gas volume is thus directly proportional to the number of moles.
- Gay-Lussac's law and Avogadro's law can be used to show that molecules of the reactive elemental gases are diatomic.
- The volume occupied by one mole of an ideal gas at STP is called the standard molar volume. The standard molar volume of an ideal gas is 22.414 10 L at standard temperature and pressure.

Vocabulary

Avogadro's law (334) Gay-Lussac's law of combining volumes of gases (333) standard molar volume of a gas (335)

11-2

- Charles's law, Boyle's law, and Avogadro's law can be combined to create the ideal gas law. The ideal gas law is stated mathematically as follows.

$$PV = nRT$$

- The value and units of the ideal gas constant depend on the units of the variables used in the ideal gas law.
- The ideal gas law can be used to calculate gas pressure, volume, temperature, or number of moles when three of these four variables are known and the gas sample does not undergo a change in conditions.
- The ideal gas law can also be used to calculate the density or molar mass of a gas sample.

Vocabulary

ideal gas constant (342) ideal gas law (340)

11-3

- Given a balanced equation and the volume of a reacting gas, the volume of another gaseous product or reactant can be calculated using their volume ratios, as long as reactants and products exist under the same conditions.
- Given the volume of a reactant or product gas, the mass of a second reactant or product can be calculated using the ideal gas law and mole-to-mass conversion factors.
- If the mass of a substance is known, the ideal gas law and the proper mass-to-mole conversion factors can be used to calculate the volume of a gas.

11-4

- Graham's law of effusion states that the relative rates of effusion of gases at the same temperature and pressure are inversely proportional to the square roots of their molar masses.
- Graham's law reflects the fact that less massive molecules effuse faster than do more massive ones.
- Graham's law can be used to compare the rates of effusion of gases at the same temperature and pressure.
- Given the relative rates of effusion of two gases and the identity of one of them, Graham's law can be used to estimate the molar mass of the other.

Vocabulary

Graham's law of effusion (352)

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REVIEWING CONCEPTS

1. a. What restrictions are there on the use of Gay-Lussac's law of combining volumes?
b. At the same temperature and pressure, what is the relationship between the volume of a gas and the number of molecules present? (11-1)

2. According to Avogadro,
a. what is the relationship between gas volume and number of moles at constant temperature and pressure?
b. what is the mathematical expression denoting this relationship? (11-1)

3. What is the relationship between the number of molecules and the mass of 22.4 L of different gases at STP? (11-1)

4. Why must the temperature and pressure be specified when stating gas density values? (11-1)

5. a. Write the equation for the ideal gas law.
b. What relationship is expressed in the ideal gas law? (11-2)

6. a. In what situation does the ideal gas law apply?
b. Why do you have to pay particular attention to units when using this law? (11-2)

7. a. In a balanced chemical equation, what is the relationship between the molar ratios and the volume ratios of gaseous reactants and products?
b. What restriction applies to the use of the volume ratios in solving stoichiometry problems? (11-3)

8. a. Distinguish between diffusion and effusion.
b. At a given temperature, what factor determines the rates at which different molecules undergo these processes? (11-4)

PROBLEMS

Molar Volume and Gas Density

9. Suppose a 5.00 L sample of O_2 at a given temperature and pressure contains 1.08×10^{23} molecules. How many molecules would be contained in each of the following at the same temperature and pressure?
a. 5.00 L H_2
b. 5.00 L CO_2
c. 10.00 L NH_3

10. How many molecules are contained in each of the following?
a. 1.00 mol O_2
b. 2.50 mol He
c. 0.0650 mol NH_3
d. 11.5 g NO_2

11. Find the mass of each of the following.
a. 2.25 mol Cl_2
b. 3.01×10^{23} molecules H_2S
c. 25.0 molecules SO_2

12. What is the volume, in liters, of each of the following at STP? (Hint: See Sample Problem 11-1.)
a. 1.00 mol O_2
b. 3.50 mol F_2
c. 0.0400 mol CO_2
d. 1.20×10^{-6} mol He

13. How many moles are contained in each of the following at STP?
a. 22.4 L N_2
b. 5.60 L Cl_2
c. 0.125 L Ne
d. 70.0 mL NH_3

14. Find the mass, in grams, of each of the following at STP. (Hint: See Sample Problem 11-2.)
a. 11.2 L H_2
b. 2.80 L CO_2
c. 15.0 mL SO_2
d. 3.40 cm^3 F_2

15. Find the volume, in liters, of each of the following at STP.
a. 8.00 g O_2
b. 3.50 g CO
c. 0.0170 g H_2S
d. 2.25×10^5 kg NH_3

Ideal Gas Law

16. Calculate the pressure, in atmospheres, exerted by each of the following. (Hint: See Sample Problem 11-3.)
a. 2.50 L of HF containing 1.35 mol at 320. K
b. 4.75 L of NO_2 containing 0.86 mol at 300. K
c. 7.50×10^2 mL of CO_2 containing 2.15 mol at 57°C

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17. Calculate the volume, in liters, occupied by each of the following. (Hint: See Sample Problem 11-4.)
a. 2.00 mol of H_2 at 300. K and 1.25 atm
b. 0.425 mol of NH_3 at 37°C and 0.724 atm
c. 4.00 g of O_2 at 57°C and 0.888 atm

18. Determine the number of moles of gas contained in each of the following.
a. 1.25 L at 250. K and 1.06 atm
b. 0.80 L at 27°C and 0.925 atm
c. 7.50×10^2 mL at –50.°C and 0.921 atm

19. Find the mass of each of the following. (Hint: See Sample Problem 11-5.)
a. 5.60 L of O_2 at 1.75 atm and 250. K
b. 3.50 L of NH_3 at 0.921 atm and 27°C
c. 125 mL of SO_2 at 0.822 atm and –53°C

20. Find the molar mass of each gas measured at the specified conditions. (Hint: See Sample Problem 11-6.)
a. 0.650 g occupying 1.12 L at 280. K and 1.14 atm
b. 1.05 g occupying 2.35 L at 37°C and 0.840 atm
c. 0.432 g occupying 7.50×10^2 mL at –23°C and 1.03 atm

21. If the density of an unknown gas is 3.20 g/L at –18°C and 2.17 atm, what is the molar mass of this gas?

22. One method of estimating the temperature of the center of the sun is based on the assumption that the center consists of gases that have an average molar mass of 2.00 g/mol. If the density of the center of the sun is 1.40 g/cm^3 at a pressure of 1.30×10^9 atm, calculate the temperature in degrees Celsius.

Gas Stoichiometry

23. Carbon monoxide reacts with oxygen to produce carbon dioxide. If 1.0 L of carbon monoxide reacts with oxygen,
a. how many liters of oxygen are required? (Hint: See Sample Problem 11-7.)
b. how many liters of carbon dioxide are produced?

24. Acetylene gas, C_2H_2, undergoes combustion to produce carbon dioxide and water vapor. If 75.0 L of CO_2 are produced,
a. how many liters of C_2H_2 are required?
b. what volume of H_2O vapor is produced?
c. what volume of O_2 is required?

25. If liquid carbon disulfide reacts with 4.50×10^2 mL of oxygen to produce the gases carbon dioxide and sulfur dioxide, what volume of each product is produced?

26. Assume that 5.60 L of H_2 at STP react with CuO according to the following equation:
$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$
Make sure the equation is balanced before beginning your calculations.
a. How many moles of H_2 react? (Hint: See Sample Problem 11-8.)
b. How many moles of Cu are produced?
c. How many grams of Cu are produced?

27. Solid iron(III) hydroxide decomposes to produce iron(III) oxide and water vapor. If 0.75 L of water vapor is produced at STP,
a. how many grams of iron(III) hydroxide were used?
b. how many grams of iron(III) oxide are produced?

28. If 29.0 L of methane, CH_4, undergoes complete combustion at 0.961 atm and 20°C, how many liters of each product are formed?

29. If air is 20.9% oxygen by volume,
a. how many liters of air are needed for complete combustion of 25.0 L of octane vapor, C_8H_{18}?
b. what volume of each product is produced?

30. A modified Haber process for making ammonia is conducted at 550.°C and 2.50×10^2 atm. If 10.0 kg of nitrogen (the limiting reactant) is used and the process goes to completion, what volume of ammonia is produced?

31. When liquid nitroglycerin, $C_3H_5(NO_3)_3$, explodes, the products are carbon dioxide, nitrogen, oxygen, and water vapor. If 5.00×10^2 g of nitroglycerin explode at STP, what is the total volume, at STP, for all gases produced?

32. The principal source of sulfur on Earth is deposits of free sulfur occurring mainly in volcanically active regions. The sulfur was initially formed by the reaction between the two volcanic vapors SO_2 and H_2S to form $H_2O(l)$ and $S_8(s)$. What volume of each gas, at 0.961 atm and 22°C, was needed to form a sulfur deposit of 4.50×10^5 kg on the slopes of a volcano in Hawaii?

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33. A 3.25 g sample of solid calcium carbide, CaC_2, reacted with water to produce acetylene gas, C_2H_2, and aqueous calcium hydroxide. If the acetylene was collected over water at 17°C and 0.974 atm, how many milliliters of acetylene were produced?

34. Balance the following chemical equation.
$Mg(s) + O_2(g) \longrightarrow MgO(s)$
Then, based on the quantity of reactant or product given, determine the corresponding quantities of the specified reactants or products, assuming that the system is at STP.
a. 22.4 L O_2 = ___ mol O_2 ⟶ ___ mol MgO
b. 11.2 L O_2 = ___ mol O_2 ⟶ ___ mol MgO
c. 1.40 L O_2 = ___ mol O_2 ⟶ ___ mol MgO

35. Assume that 8.50 L of I_2 are produced using the following reaction that takes place at STP:
$KI(aq) + Cl_2(g) \longrightarrow KCl(aq) + I_2(g)$
Balance the equation before beginning your calculations.
a. How many moles of I_2 are produced?
b. How many moles of KI were used?
c. How many grams of KI were used?

36. Suppose that 6.50×10^2 mL of hydrogen gas are produced through a replacement reaction involving solid iron and sulfuric acid, H_2SO_4, at STP. How many grams of iron(II) sulfate are also produced?

37. Methanol, CH_3OH, is made by causing carbon monoxide and hydrogen gases to react at high temperature and pressure. If 4.50×10^2 mL of CO and 825 mL of H_2 are mixed,
a. which reactant is present in excess?
b. how much of that reactant remains after the reaction?
c. what volume of CH_3OH is produced, assuming the same pressure?

38. Assume that 13.5 g of Al react with HCl according to the following equation, at STP:
$Al(s) + HCl(aq) \longrightarrow AlCl_3(aq) + H_2(g)$
Remember to balance the equation first.
a. How many moles of Al react?
b. How many moles of H_2 are produced?
c. How many liters of H_2 at STP are produced? (Hint: See Sample Problem 11-9.)

Effusion and Diffusion

39. Quantitatively compare the rates of effusion for the following pairs of gases at the same temperature and pressure.
a. hydrogen and nitrogen (Hint: See Sample Problem 11-10.)
b. fluorine and chlorine

40. What is the ratio of the average velocity of hydrogen molecules to that of neon atoms at the same temperature and pressure?

41. At a certain temperature and pressure, chlorine molecules have an average velocity of 0.0380 m/s. What is the average velocity of sulfur dioxide molecules under the same conditions?

42. A sample of helium effuses through a porous container 6.50 times faster than does unknown gas X. What is the molar mass of the unknown gas?

MIXED REVIEW

43. An unknown gas effuses at 0.850 times the effusion rate of nitrogen dioxide, NO_2. Estimate the molar mass of the unknown gas.

44. Use the ideal gas law, $PV = nRT$, to derive Boyle's law and Charles's law.

45. A container holds 265 mL of chlorine gas, Cl_2. Assuming that the gas sample is at STP, what is its mass?

46. Suppose that 3.11 mol of carbon dioxide is at a pressure of 0.820 atm and a temperature of 39°C. What is the volume of the sample, in liters?

47. Compare the rates of diffusion of carbon monoxide, CO, and sulfur trioxide, SO_3.

48. A gas sample that has a mass of 0.993 g occupies 0.570 L. Given that the temperature is 281 K and the pressure is 1.44 atm, what is the molar mass of the gas?

49. The density of a gas is 3.07 g/L at STP. Calculate the gas's molar mass.

50. How many moles of helium gas would it take to fill a gas balloon with a volume of 1000. cm^3 when the temperature is 32°C and the atmospheric pressure is 752 mm Hg?

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51. A gas sample is collected at 16°C and 0.982 atm. If the sample has a mass of 7.40 g and a volume of 3.96 L, find the volume of the gas at STP and the molar mass.

CRITICAL THINKING

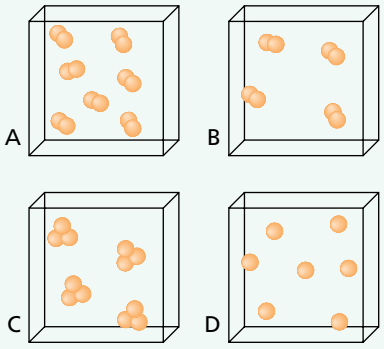
52. Evaluating Methods In solving a problem, what types of conditions involving temperature, pressure, volume, or number of moles would allow you to use
a. the combined gas law?
b. the ideal gas law?

53. Relating Ideas Write expressions relating the rates of effusion, molar masses, and densities of two different gases, A and B.

54. Evaluating Ideas Gay-Lussac's law of combining volumes holds true for relative volumes at any proportionate size. Use Avogadro's law to explain why this proportionality exists.

55. Designing Experiments Design an experiment to prove that the proportionality described in item 54 exists.

56. Interpreting Concepts The diagrams that follow represent equal volumes of four different gases.



Use the diagrams to answer the following questions:
a. Are these gases at the same temperature and pressure? How do you know?
b. If the molar mass of gas B is 38 g/mol and that of gas C is 46 g/mol, which gas sample is more dense?
c. To make the densities of gas samples B and C equal, which gas should expand in volume?
d. If the densities of gas samples A and C are equal, what is the relationship between their molecular masses?

TECHNOLOGY & LEARNING

57. Graphing Calculator Calculating Pressure Using the Ideal Gas Law

The graphing calculator can run a program that calculates the pressure in atmospheres, given the number of moles of a gas (n), volume (V), and temperature (T). Given a 0.50 mol gas sample with a volume of 10. L at 298 K, you can calculate the pressure according to the ideal gas law. Begin by using the program to carry out the calculation. Next, use it to make calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

Note: Answers are written with five significant figures.

a. What is the pressure for a gas with an amount of 1.3 mol, volume of 8.0 L, and temperature of 293 K?
b. What is the pressure for a gas with an amount of 2.7 mol, volume of 8.5 L, and temperature of 310 K?
c. A gas with an amount of 0.75 mol and a volume of 6.0 L is measured at two different temperatures: 300 K and 275 K. At which temperature is the pressure greater?

HANDBOOK SEARCH

58. Most elements from Groups 1, 2, and 13 will react with water, acids, or bases to produce hydrogen gas. Review the common reactions information in the *Elements Handbook* and answer the following:
a. Write the equation for the reaction of barium with water.

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b. Write the equation for the reaction between cesium and hydrochloric acid.
c. Write the equation for the reaction of gallium with hydrofluoric acid.
d. What mass of barium would be needed to react with excess water to produce 10.1 L of H_2 at STP?
e. What masses of cesium and hydrochloric acid would be required to produce 10.1 L of H_2 at STP?

59. Group 1 metals react with oxygen to produce oxides, peroxides, or superoxides. Review the equations for these common reactions in the *Elements Handbook* and answer the following:
a. How do oxides, peroxides, and superoxides differ?
b. What mass of product will be formed from a reaction of 5.00 L of oxygen with excess sodium? The reaction occurs at 27°C and 1 atm.

60. Most metals react with chlorine from Group 17 to produce salts. Review these common reactions in the *Elements Handbook* and answer the following:
a. Write the equation for the reaction of iron and chlorine gas.
b. What mass of iron salt is produced if an excess of iron reacts with 450. mL of chlorine gas at 27°C and 1 atm?

RESEARCH & WRITING

61. How do scuba divers use the laws and principles that describe the behavior of gases to their advantage? What precautions do they take to prevent the bends?

62. Explain the processes involved in the liquefaction of gases. What substances that are gases under normal room conditions are typically used in the liquid form? Why?

63. Research the relationship between explosives and the establishment of Nobel Prizes. Prepare a report that describes your findings.

64. Write a summary describing how Gay-Lussac's work on combining volumes relates to Avogadro's study of gases. Explain how certain conclusions about gases followed logically from consideration of the work of both scientists.

ALTERNATIVE ASSESSMENT

65. During a typical day, record every instance in which you encounter the diffusion or effusion of gases (for example, smelling perfume).

66. **Performance** Qualitatively compare the molecular masses of various gases by noting how long it takes you to smell them from a fixed distance. Work only with materials that are not dangerous, such as flavor extracts, fruit peels, and onions.

67. **Performance** Design an experiment to gather data to verify the Ideal Gas Law. If your teacher approves of your plan, carry it out. Illustrate your data with a graph, and determine if the data are consistent with the Ideal Gas Law.

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CHAPTER 12

Liquids and Solids

Courtesy of the artist and Galerie Lelong, New York

The total three-dimensional arrangement of particles of a crystal is its crystal structure.

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Liquids

SECTION 12-1

Objectives

- Describe the motion of particles in liquids and the properties of liquids according to the kinetic-molecular theory.
- Discuss the process by which liquids can change into a gas. Define *vaporization.*
- Discuss the process by which liquids can change into a solid. Define *freezing.*

The water in the waves crashing on a beach and the molten lava rushing down the sides of a volcano are examples of matter in the liquid state. When you think of Earth's oceans, lakes, and rivers and the many liquids you use every day, it is hard to believe that liquids are the *least* common state of matter in the universe. Liquids are less common than solids, gases, and plasmas because a substance in the liquid state can exist only within a relatively narrow range of temperatures and pressures.

In this section, you will examine the properties of the liquid state. You will also compare them with those of the solid state and the gas state. These properties will be discussed in terms of the kinetic-molecular theory.

Properties of Liquids and the Kinetic-Molecular Theory

A liquid can be described as a form of matter that has a definite volume and takes the shape of its container. The properties of liquids can be understood by applying the kinetic-molecular theory, considering the motion and arrangement of molecules and the attractive forces between them.

As in a gas, particles in a liquid are in constant motion. However, the particles in a liquid are closer together and lower in kinetic energy than those in a gas. Therefore, the attractive forces between particles in a liquid are more effective than those between particles in a gas. This attraction between liquid particles is caused by the intermolecular forces discussed in Chapter 6: dipole-dipole forces, London dispersion forces, and hydrogen bonding.

Liquids are more ordered than gases because of the stronger intermolecular forces and the lower mobility of the liquid particles. According to the kinetic-molecular theory of liquids, the particles are not bound together in fixed positions. Instead, they move about constantly. This particle mobility explains why liquids and gases are referred to as fluids. *A* **fluid** *is a substance that can flow and therefore take the shape of its container.* Most liquids naturally flow downhill because of gravity. However, some liquids can flow in other directions as well. For example, liquid helium near absolute zero has the unusual property of being able to flow uphill.

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Module 1: States of Matter/Classes of Matter

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***sci*LINKS CODE:** HC2121

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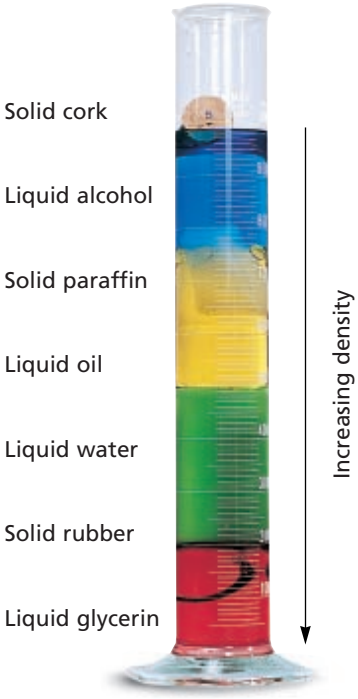


FIGURE 12-1 Solids and liquids of different densities are shown. The densest materials are at the bottom. The least dense are at the top. (Dyes have been added to the liquids to make the layers more visible.)

Relatively High Density

At normal atmospheric pressure, most substances are thousands of times denser as liquids than as gases. This higher density is a result of the close arrangement of liquid particles. Most substances are only slightly less dense (about 10%) as liquids than as solids, however. Water is one of the few substances that becomes less dense when it solidifies, as will be discussed further in Section 12-4.

At the same temperature and pressure, different liquids can differ greatly in density. Figure 12-1 shows some liquids and solids with different densities. The densities differ to such an extent that the liquids form layers.

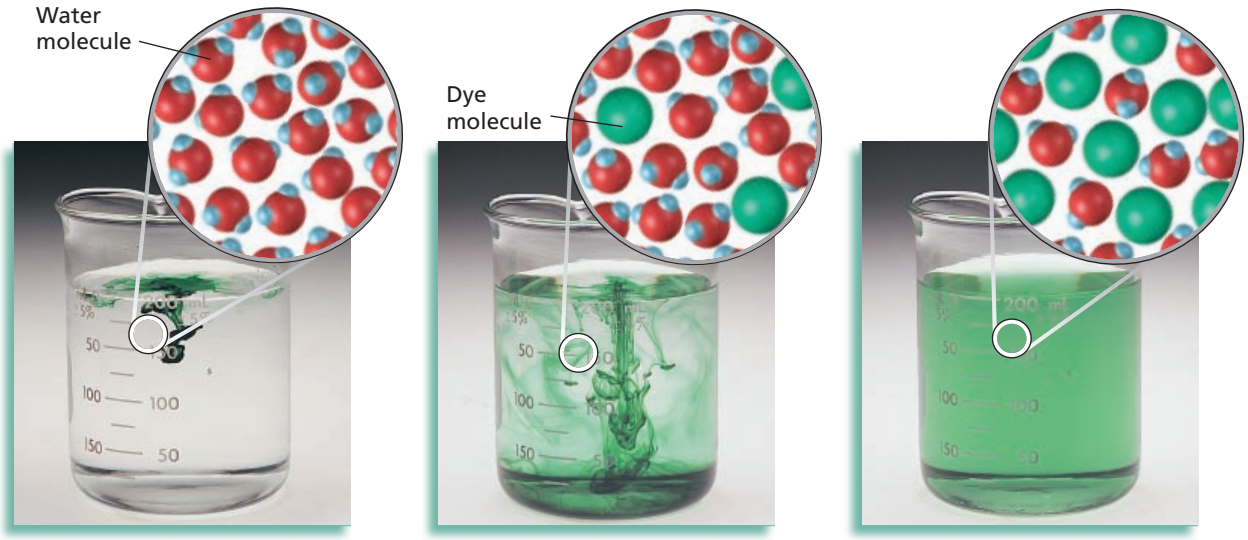
Relative Incompressibility

When liquid water at 20°C is compressed by a pressure of 1000 atm, its volume decreases by only 4%. Such behavior is typical of all liquids and is similar to the behavior of solids. In contrast, a gas under a pressure of 1000 atm would have only about 1/1000 of its volume at normal atmospheric pressure. Liquids are much less compressible than gases because liquid particles are more closely packed together. In addition, liquids can transmit pressure equally in all directions.

Ability to Diffuse

As described in Chapter 10, gases diffuse and mix with other gas particles. Liquids also diffuse and mix with other liquids, as shown in Figure 12-2. Any liquid gradually diffuses throughout any other liquid in which it can dissolve. As in gases, diffusion in liquids occurs because of the constant, random motion of particles. Yet diffusion is much slower in liquids than in gases because liquid particles are closer together. Also, the attractive forces between the particles of a liquid slow their movement. As the temperature of a liquid is increased, diffusion occurs more rapidly. That is because the average kinetic energy, and therefore the average speed of the particles, is increased.

FIGURE 12-2 Like gases, the two liquids in this beaker diffuse over time. The green liquid food coloring from the drop will eventually form a uniform solution with the water.



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Surface Tension

A property common to all liquids, **surface tension,** *is a force that tends to pull adjacent parts of a liquid's surface together, thereby decreasing surface area to the smallest possible size.* Surface tension results from the attractive forces between particles of a liquid. The higher the force of attraction, the higher the surface tension. Water has a higher surface tension than most liquids. This is due to the hydrogen bonds water molecules can form with each other. The molecules at the surface of the water are a special case. They can form hydrogen bonds with the other water molecules beneath them and beside them, but not with the molecules in the air above them. As a result, the surface water molecules are drawn together and toward the body of the liquid, creating a high surface tension. Surface tension causes liquid droplets to take on a spherical shape because a sphere has the smallest possible surface area for a given volume. An example of this phenomenon is shown in Figure 12-3.

Capillary action, *the attraction of the surface of a liquid to the surface of a solid,* is a property closely related to surface tension. A liquid will rise quite high in a very narrow tube if a strong attraction exists between the liquid molecules and the molecules that make up the surface of the tube. This attraction tends to pull the liquid molecules upward along the surface against the pull of gravity. This process continues until the weight of the liquid balances the gravitational force. Capillary action can occur between water molecules and paper fibers, as shown in Figure 12-4. Capillary action is at least partly responsible for the transportation of water from the roots of a plant to its leaves. The same process is responsible for the concave liquid surface, called a *meniscus,* that forms in a test tube or graduated cylinder.

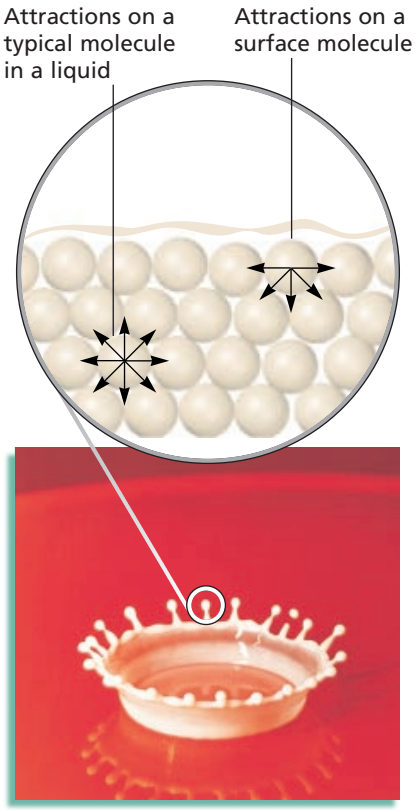

FIGURE 12-3 As a result of surface tension, liquids form roughly spherical drops. The net attractive forces between the particles pull the molecules on the surface inward and closer together than those farther down in the liquid, minimizing the surface area.

Evaporation and Boiling

The process by which a liquid or solid changes to a gas is **vaporization.** Evaporation is a form of vaporization. **Evaporation** *is the process by which particles escape from the surface of a nonboiling liquid and enter the gas state.*

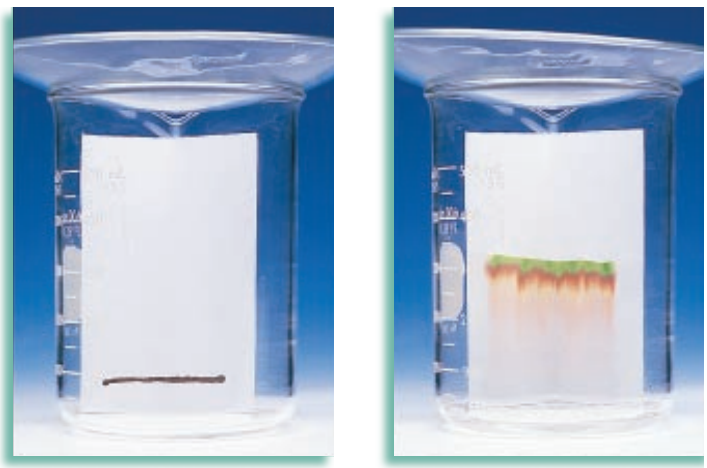

FIGURE 12-4 The attraction between polar water molecules and polar cellulose molecules in paper fibers causes the water to move up in the paper. The water-soluble ink placed near the bottom of the paper in (a) rises up the paper along with the water, as seen in (b). As the ink moves up the paper, it is separated into its various components, producing the different bands of color. This separation occurs because the water and the paper attract the molecules of the ink components differently. These phenomena are used in the separation process of paper chromatography seen here.

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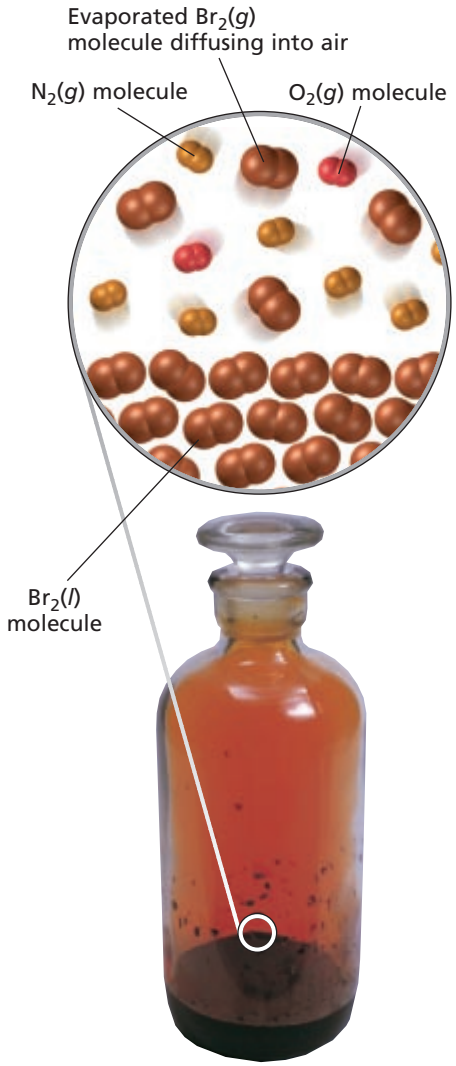

FIGURE 12-5 Liquid bromine, Br_2, evaporates near room temperature. The resulting brownish red gas diffuses into the air above the surface of the liquid.

A small amount of liquid bromine was added to the bottle shown in Figure 12-5. Within a few minutes, the air above the liquid bromine turned brownish-red. That is because some bromine molecules escaped from the surface of the liquid. They have changed into the gas state, becoming bromine vapor, which mixed with the air. A similar phenomenon occurs if you apply perfume to your wrist. Within seconds, you become aware of the perfume's fragrance. Scent molecules evaporate from your skin and diffuse through the air, to be detected by your nose.

Evaporation occurs because the particles of a liquid have different kinetic energies. Particles with higher-than-average energies move faster. Some surface particles with higher-than-average energies can overcome the intermolecular forces that bind them to the liquid. They can then escape into the gas state.

Evaporation is a crucial process in nature. Evaporation removes fresh water from the surface of the ocean, leaving behind a higher concentration of salts. In subtropical areas, evaporation occurs at a higher rate, causing the surface water to be saltier. All water that falls to Earth in the form of rain and snow previously evaporated from oceans, lakes, and rivers. Evaporation of perspiration plays an important role in keeping you cool. Perspiration, which is mostly water, cools you by absorbing body heat when it evaporates. Heat energy is absorbed from the skin, causing the cooling effect.

Boiling is the change of a liquid to bubbles of vapor that appear throughout the liquid. Boiling differs from evaporation, as you will see in Section 12-3.

Formation of Solids

When a liquid is cooled, the average energy of its particles decreases. If the energy is low enough, attractive forces pull the particles into an even more orderly arrangement. The substance then becomes a solid. *The physical change of a liquid to a solid by removal of heat is called* **freezing** *or solidification.* Perhaps the best-known example of freezing is the change of liquid water to solid water, or ice, at 0°C. Another familiar example is the solidification of paraffin at room temperature. All liquids freeze, although not necessarily at temperatures you normally encounter. Ethanol, for example, freezes near –115°C.

SECTION REVIEW

1. Describe the liquid state according to the kinetic-molecular theory.
2. List the properties of liquids.
3. How does the kinetic-molecular theory explain the following properties of liquids? (a) their relatively high density, (b) their ability to diffuse, and (c) their ability to evaporate
4. Explain why liquids in a test tube form a meniscus.
5. Compare vaporization and evaporation.

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Solids

SECTION 12-2

OBJECTIVES

- Describe the motion of particles in solids and the properties of solids according to the kinetic-molecular theory.
- Distinguish between the two types of solids.
- Describe the different types of crystal symmetry. Define *crystal structure* and *unit cell.*

"Solid as a rock" is a common expression that suggests something that is hard or unyielding and that has a definite shape and volume. In this section, you will examine the properties of solids and compare them with those of liquids and gases. As with the other states of matter, the properties of solids are explained in terms of the kinetic-molecular theory.

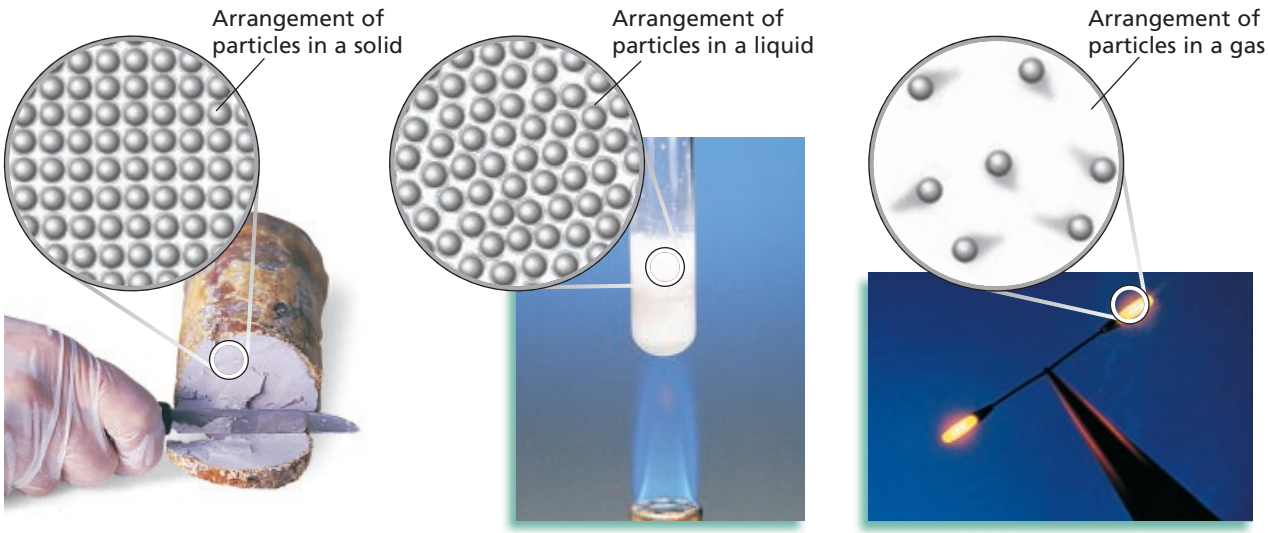
Properties of Solids and the Kinetic-Molecular Theory

The particles of a solid are more closely packed than those of a liquid or gas. Intermolecular forces between particles are therefore much more effective in solids. Dipole-dipole attractions, London dispersion forces, and hydrogen bonding exert stronger effects in solids than in the corresponding liquids or gases. These forces tend to hold the particles of a solid in relatively fixed positions, with only vibrational movement around fixed points. Because the motions of the particles are restricted in this way, solids are more ordered than liquids and are much more ordered than gases. The importance of order and disorder in physical and chemical changes will be discussed in Chapter 17. Compare the physical appearance and molecular arrangement of the element in Figure 12-6 in solid, liquid, and gas form.

CHEMISTRY INTERACTIVE TUTOR

Module 1: States of Matter/Classes of Matter

FIGURE 12-6 Particles of sodium metal in three different states are shown. Sodium exists in a gaseous state in a sodium-vapor lamp.



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There are two types of solids: crystalline solids and amorphous solids. *Most solids are* **crystalline solids**—*they consist of crystals. A* **crystal** *is a substance in which the particles are arranged in an orderly, geometric, repeating pattern.* Noncrystalline solids, including glass and plastics, are called amorphous solids. *An* **amorphous solid** *is one in which the particles are arranged randomly.* The two types of solids will be discussed in more detail later in this section.

Definite Shape and Volume

Unlike liquids and gases, solids can maintain a definite shape without a container. In addition, crystalline solids are geometrically regular. Even the fragments of a shattered crystalline solid have distinct geometric shapes that reflect their internal structure. Amorphous solids maintain a definite shape, but they do not have the distinct geometric shapes of crystalline solids. For example, glass can be molded into any shape. If it is shattered, glass fragments can have a wide variety of irregular shapes.

The volume of a solid changes only slightly with a change in temperature or pressure. Solids have definite volume because their particles are packed closely together. There is very little empty space into which the particles can be compressed. Crystalline solids generally do not flow because their particles are held in relatively fixed positions.

Definite Melting Point

Melting *is the physical change of a solid to a liquid by the addition of heat. The temperature at which a solid becomes a liquid is its* **melting point.** At this temperature, the kinetic energies of the particles within the solid overcome the attractive forces holding them together. The particles can then break out of their positions in crystalline solids, which have definite melting points. In contrast, amorphous solids, such as glass and plastics, have no definite melting point. They have the ability to flow over a range of temperatures. Therefore, amorphous solids are sometimes classified as **supercooled liquids,** *which are substances that retain certain liquid properties even at temperatures at which they appear to be solid.* These properties exist because the particles in amorphous solids are arranged randomly, much like the particles in a liquid. Unlike the particles in a true liquid, however, the particles in amorphous solids are not constantly changing their positions.

High Density and Incompressibility

In general, substances are most dense in the solid state. Solids tend to be slightly denser than liquids and much denser than gases. The higher density results from the fact that the particles of a solid are more closely packed than those of a liquid or a gas. Solid hydrogen is the least dense solid; it has a density of about 1/320 of the densest element, osmium, Os.

Solids are generally less compressible than liquids. For practical purposes, solids can be considered incompressible. Some solids, such as wood and cork, may *seem* compressible, but they are not. They contain pores that are filled with air. When subjected to intense pressure, the pores are compressed, not the wood or cork itself.

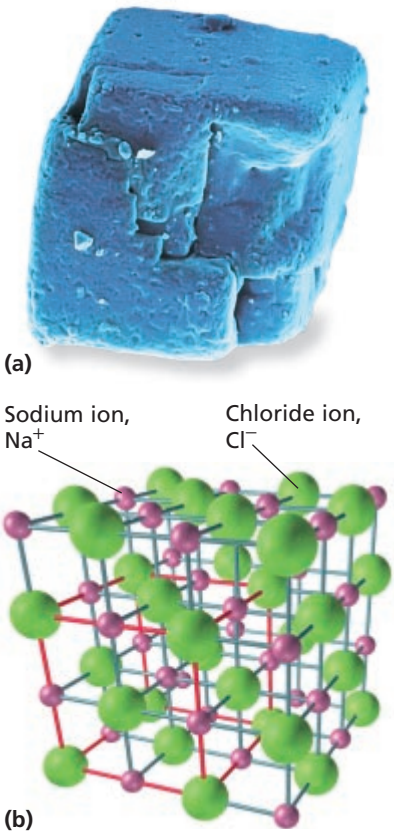

FIGURE 12-7 (a) This is a scanning electron micrograph (SEM) of a sodium chloride crystal. A sodium chloride crystal can be represented by its crystal structure (b), which is made up of individual unit cells represented regularly in three dimensions. Here, one unit cell is outlined in red.

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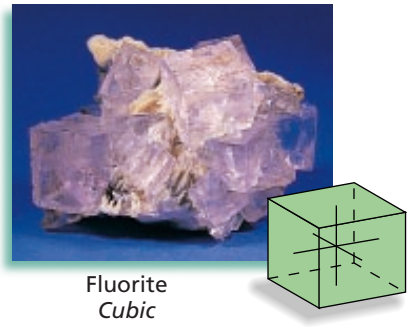
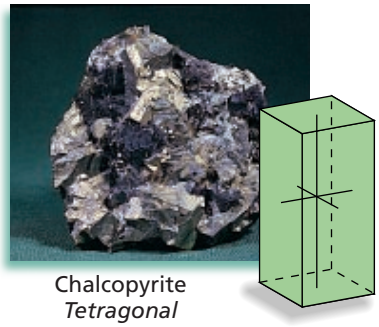
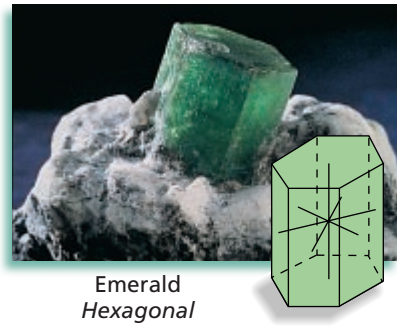
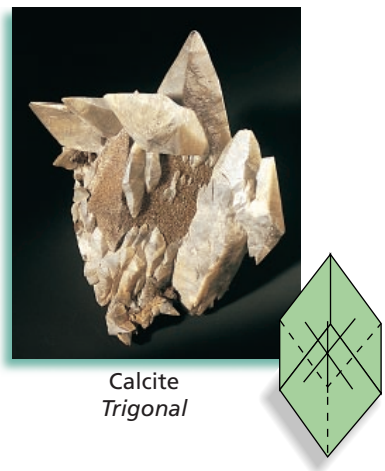
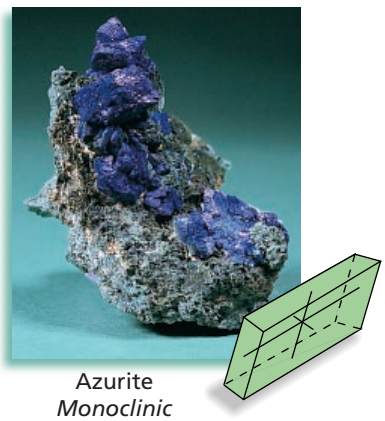

Fluorite
Cubic


Chalcopyrite
Tetragonal


Emerald
Hexagonal


Calcite
Trigonal

Aragonite
Orthorhombic


Azurite
Monoclinic

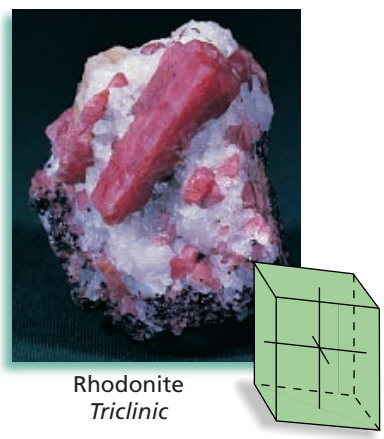

Rhodonite
Triclinic

FIGURE 12-8 Shown are the seven basic crystalline systems and representative minerals of each.

Low Rate of Diffusion

If a zinc plate and a copper plate are clamped together for a long time, a few atoms of each metal will diffuse into the other. This observation shows that diffusion does occur in solids. The rate of diffusion is millions of times slower in solids than in liquids, however.

Crystalline Solids

Crystalline solids exist either as single crystals or as groups of crystals fused together. *The total three-dimensional arrangement of particles of a crystal is called a* **crystal structure.** The arrangement of particles in the crystal can be represented by a coordinate system called a lattice. *The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice is called a* **unit cell.** Each crystal lattice contains many unit cells packed together. Figure 12-7 shows the relationship between a crystal lattice and its unit cell. A crystal and its unit cells can have any one of seven types of symmetry. This fact enables scientists to classify crystals by their shape. Diagrams and examples of each type of crystal symmetry are shown in Figure 12-8.

Binding Forces in Crystals

Crystal structures can also be described in terms of the types of particles in them and the types of chemical bonding between the particles.

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TABLE 12-1 *Melting and Boiling Points of Representative Crystalline Solids*

Type of substance	Formula	Melting point (°C)	Boiling point at 1 atm (°C)
Ionic	NaCl	801	1413
	MgF_2	1266	2239
Covalent network	$(SiO_2)_x$	1610	2230
	C_x (diamond)	3500	3930
Metallic	Hg	–39	357
	Cu	1083	2567
	Fe	1535	2750
	W	3410	5660
Covalent molecular (nonpolar)	H_2	–259	–253
	O_2	–218	–183
	CH_4	–182	–164
	CCl_4	–23	77
	C_6H_6	6	80
Covalent molecular (polar)	NH_3	–78	–33
	H_2O	0.	100.

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According to this method of classification, there are four types of crystals. These types are listed in Table 12-1. Refer to this table as you read the following discussion.

1. *Ionic crystals.* As discussed in Chapter 6, the ionic crystal structure consists of positive and negative ions arranged in a regular pattern. The ions can be monatomic or polyatomic. Generally, ionic crystals form when Group-1 or Group-2 metals combine with Group-16 or Group-17 nonmetals or nonmetallic polyatomic ions. The strong binding forces between the positive and negative ions in the crystal structure give the ionic crystals certain properties. For example, these crystals are hard and brittle, have high melting points, and are good insulators.
2. *Covalent network crystals.* In covalent network crystals, the sites contain single atoms. Each atom is covalently bonded to its nearest neighboring atoms. The covalent bonding extends throughout a network that includes a very large number of atoms. Three-dimensional covalent network solids include diamond, C_x, quartz, $(SiO_2)_x$—shown in Figure 12-9—silicon carbide, $(SiC)_x$, and many oxides of transition metals. Such solids are essentially giant molecules. The subscript x in these formulas indicates that the component within the parentheses extends indefinitely. The network solids are nearly always very hard and brittle. They have rather high melting points and are usually nonconductors or semiconductors.
3. *Metallic crystals.* As discussed in Chapter 6, the metallic crystal structure consists of metal atoms surrounded by a sea of valence electrons. The electrons are donated by the metal atoms and belong to

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the crystal as a whole. The freedom of the outer-structure electrons to move throughout the crystal explains the high electric conductivity of metals. As you can see from Table 12-1, the melting points of different metallic crystals vary greatly.

4. *Covalent molecular crystals.* The crystal structure of a covalent molecular substance consists of covalently bonded molecules held together by intermolecular forces. If the molecules are nonpolar—for example, hydrogen, H_2, methane, CH_4, and benzene, C_6H_6—then there are only weak London dispersion forces between molecules. In a polar covalent molecular crystal—for example, water, H_2O, and ammonia, NH_3—molecules are held together by dispersion forces, by somewhat stronger dipole-dipole forces, and sometimes by even stronger hydrogen bonding. The forces that hold polar or nonpolar molecules together in the structure are much weaker than the covalent chemical bonds between the atoms within each molecule. Covalent molecular crystals thus have low melting points. They are easily vaporized, are relatively soft, and are good insulators. Ice crystals, the most familiar molecular crystals, are discussed in Section 12-4.

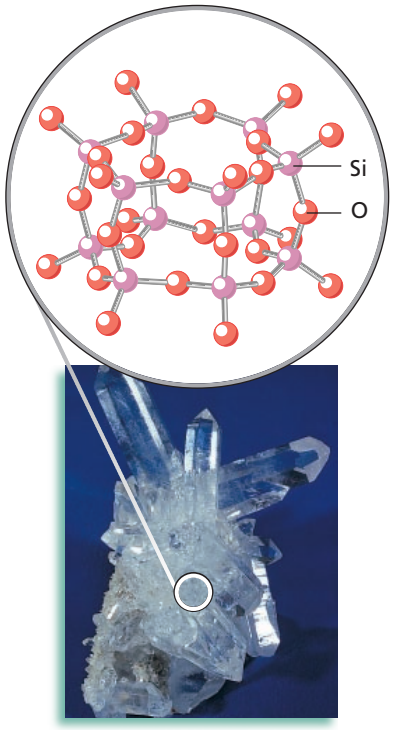

FIGURE 12-9 Covalent network crystals include three-dimensional network solids, such as this quartz, $(SiO_2)_x$, shown here with its three-dimensional atomic structure.

Amorphous Solids

The word *amorphous* comes from the Greek for "without shape." Unlike crystals, amorphous solids do not have a regular, natural shape.

Amorphous solids tend to hold their shape for a long time. However, some amorphous solids do flow, although usually very slowly. Some samples of very old window glass are thicker at the bottom than at the top suggesting that the glass has flowed downward over the years. Glasses make up a distinctive group of amorphous solids. They are made by cooling certain molten materials in such a way that they do not crystallize but remain amorphous.

There are hundreds of types of plastic and glass, all of which have thousands of important applications. Glass is used for everything from fiberglass automobile bodies to optical fibers that use light to transmit telephone conversations.

SECTION REVIEW

1. Describe the solid state according to the kinetic-molecular theory.
2. What is the difference between an amorphous solid and a crystalline solid?
3. Account for each of the following properties of solids: (a) the definite volume, (b) the relatively high density of solids, (c) the extremely low rate of diffusion.
4. Compare and contrast the four types of crystals.

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SECTION 12-3

Changes of State

Objectives

- Explain the relationship between equilibrium and changes of state.
- Predict changes in equilibrium using Le Châtelier's principle.
- Explain what is meant by equilibrium vapor pressure.
- Describe the processes of boiling, freezing, melting, and sublimation.
- Interpret phase diagrams.

CHEMISTRY INTERACTIVE TUTOR

Module 1: States of Matter/ Classes of Matter
Module 7: Equilibrium

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Matter on Earth can exist in any of these states—gas, liquid, or solid—and can change from one state to another. Table 12-2 lists the possible changes of state. In this section, you will examine these changes of state and the factors that determine them.

Equilibrium

Equilibrium *is a dynamic condition in which two opposing changes occur at equal rates in a closed system.* In a closed system, matter cannot enter or leave, but energy can. Both matter and energy can escape or enter an open system. For example, sunlight, heat from a burner, or cooling by ice can cause energy to enter or leave a system.

For an analogy of equilibrium, think of a public swimming pool on a summer day. In the morning, more people enter the pool than leave to go home. The pool gets more and more crowded. This system is not in equilibrium. Later in the day, the number of people entering and leaving will be the same. While the total number of people in the pool stays the same for a long time, individuals are constantly coming and going. The system is in equilibrium.

Equilibrium is a very important chemical concept. Here you will learn about it in relation to changes of state. In Chapter 18, you will study equilibrium in terms of chemical reactions.

Equilibrium and Changes of State

Consider the evaporation of water in a closed container in which there is initially a vacuum over the liquid, as illustrated in Figure 12-10.

TABLE 12-2 *Possible Changes of State*

Change of state	Process	Example
Solid ⟶ liquid	melting	ice ⟶ water
Solid ⟶ gas	sublimation	dry ice ⟶ CO_2 gas
Liquid ⟶ solid	freezing	water ⟶ ice
Liquid ⟶ gas	vaporization	liquid bromine ⟶ bromine vapor
Gas ⟶ liquid	condensation	water vapor⟶ water
Gas ⟶ solid	deposition	water vapor ⟶ ice

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FIGURE 12-10 A liquid-vapor equilibrium develops in a closed system. (a) At first there is only liquid present, but molecules are beginning to evaporate. (b) Evaporation continues at a constant rate. Some vapor molecules are beginning to condense to liquid. (c) Equilibrium has been reached between the rate of condensation and the rate of evaporation.

Assume that the contents of the container maintain the same temperature as the surroundings, approximately 25°C. The water and the container are the system. Initially, there is a single phase inside this system—the liquid phase. *A* **phase** *is any part of a system that has uniform composition and properties.*

If the energy of a water molecule at the upper surface of the liquid is high enough, the molecule can overcome the attraction of neighboring molecules, leave the liquid phase, and evaporate. Water molecules that have entered the vapor phase behave as typical gas molecules. Some of these vapor molecules move down toward the liquid surface and condense. That is, they reenter the liquid phase. **Condensation** *is the process by which a gas changes to a liquid.*

If the temperature and surface area of the liquid remain constant, the rate at which its molecules enter the vapor phase remains constant. The rate at which the water molecules pass from the vapor phase to the liquid phase depends on the concentration of molecules in the vapor phase. The concentration of vapor molecules, and therefore the rate of condensation, is initially zero, as shown in Figure 12-10(a). As time passes and evaporation continues, the concentration of vapor molecules increases. This increase in concentration results in an increase in the condensation rate. However, the rate of condensation is still lower than the rate of evaporation, as shown in Figure 12-10(b). Eventually, the concentration of vapor increases to the point at which the rate of condensation becomes equal to the rate of evaporation, as shown in Figure 12-10(c). In other words, equilibrium is reached and the amounts of liquid and of vapor now remain constant.

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An Equilibrium Equation

Whenever a liquid changes to a vapor, it absorbs heat energy from its surroundings. Evaporation can therefore be represented by the following equation.

$$\text{liquid} + \text{heat energy} \longrightarrow \text{vapor}$$

Whenever a vapor condenses, it gives off heat energy to its surroundings. Condensation can therefore be represented by the following equation.

$$\text{vapor} \longrightarrow \text{liquid} + \text{heat energy}$$

The liquid-vapor equilibrium can be represented by the following equation.

$$\text{liquid} + \text{heat energy} \rightleftharpoons \text{vapor}$$

The "double-yields" sign in the equation above represents a reversible reaction. It means that the reaction can proceed in either direction. The forward reaction is represented when the equation is read from left to right (liquid + heat energy ⟶ vapor). The reverse reaction is represented when the equation is read from right to left (vapor ⟶ liquid + heat energy).

Le Châtelier's Principle

A system will remain at equilibrium until something occurs to change this condition. It is important to understand the factors that can be used to control the equilibrium of a system. In 1888, the French chemist Henri Louis Le Châtelier developed a principle that enables us to predict how a change in conditions will affect a system at equilibrium. **Le Châtelier's principle** can be stated as follows: *When a system at equilibrium is disturbed by application of a stress, it attains a new equilibrium position that minimizes the stress.* A stress is typically a change in concentration, pressure, or temperature.

Equilibrium and Temperature

You can use Le Châtelier's principle to predict how the liquid-vapor equilibrium changes when a stress is applied in the closed container of liquid discussed earlier. For example, suppose the temperature of the system is increased from 25°C to 50°C. The equilibrium of the system can be represented by the following reversible reaction.

$$\text{liquid} + \text{heat energy} \rightleftharpoons \text{vapor}$$

According to Le Châtelier's principle, the system will respond to an increase in temperature. In this case, the forward reaction is endothermic; that is, it absorbs heat energy. The forward reaction is favored to counteract a rise in temperature and to minimize the stress applied to it (in

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this case, the change in temperature). The forward reaction proceeds at a higher rate than the reverse reaction until a new equilibrium is reached. At 50°C, the concentration of vapor is higher than it was at 25°C. However, at equilibrium, the reverse reaction, condensation, also occurs at a higher rate than it did at the lower temperature.

Suppose, on the other hand, that the temperature of the system in equilibrium at 25°C is lowered to 5°C. According to Le Châtelier's principle, the system will adjust to counteract the temperature decrease. Now the reverse reaction is favored because it is exothermic; that is, it releases heat energy. Equilibrium is shifted to the left and reestablished at 5°C. The vapor concentration is now lower than it originally was at 25°C.

Equilibrium and Concentration

Suppose the mass and temperature of this equilibrium system remain the same, but the volume suddenly increases. What happens to the equilibrium? Initially, the concentration of molecules in the vapor phase decreases because the same number of vapor-phase molecules now occupies a larger volume. Because the concentration of vapor molecules decreases, fewer vapor molecules strike the liquid surface per second and return to the liquid phase. Therefore, the rate of condensation decreases. The rate of evaporation, however, has remained the same and is therefore higher now than the rate of condensation. As a result, an additional net evaporation of liquid occurs. When a new equilibrium is finally reestablished, the concentration of molecules in the vapor phase is the same as in the lower-volume system. Because there was a net movement of molecules from the liquid phase to the vapor phase, the number of liquid molecules has decreased. The equilibrium has therefore shifted to the right. Table 12-3 summarizes the effects on the equilibrium of this liquid-vapor system caused by certain changes.

TABLE 12-3 ***Shifts in the Equilibrium for the Reaction Liquid + Heat Energy $\rightleftharpoons$ Vapor***

Change	Shift
Addition of liquid	right
Removal of liquid	left
Addition of vapor	left
Removal of vapor	right
Decrease in container volume	left
Increase in container volume	right
Decrease in temperature	left
Increase in temperature	right

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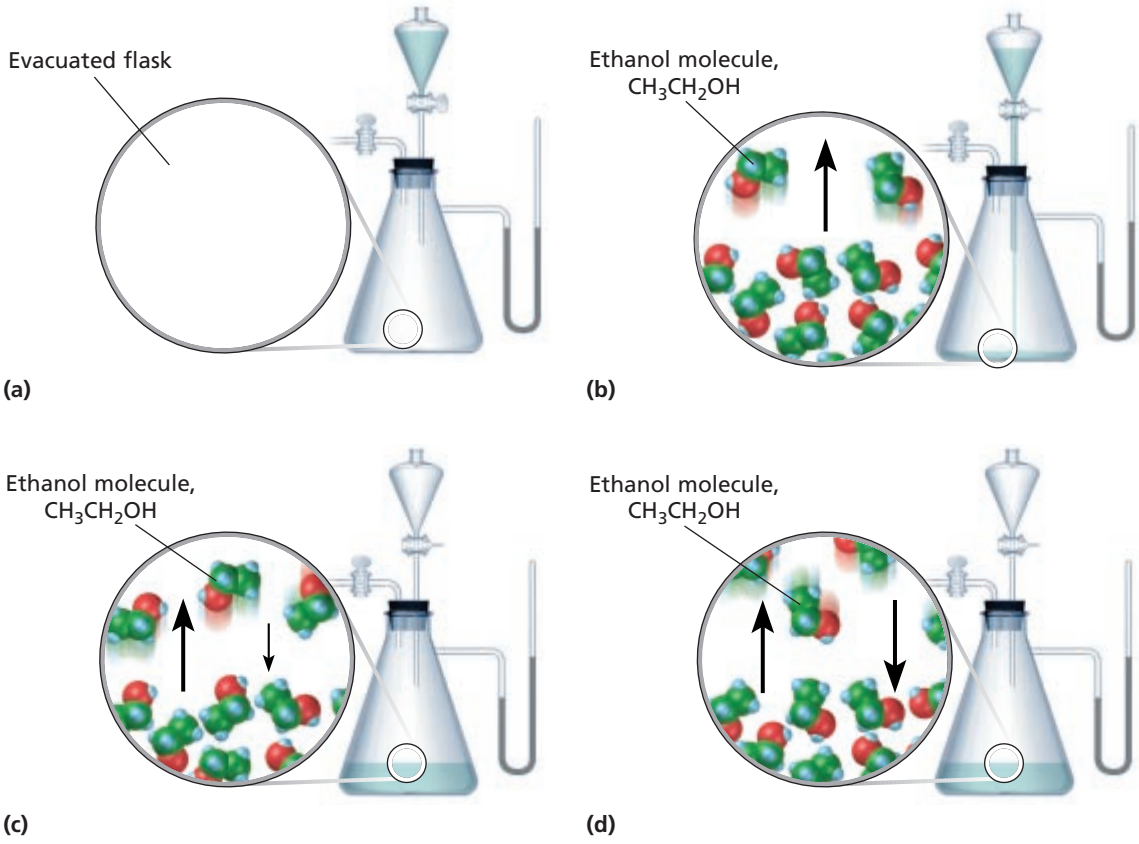

FIGURE 12-11 (a) The vapor pressure of ethanol, CH_3CH_2OH, can be measured by dispensing liquid ethanol into an evacuated flask that is part of a closed system. (b) Ethanol molecules leave the liquid surface to form vapor. (c) Molecules continue to vaporize and condense until equilibrium is reached. (d) At equilibrium, the pressure exerted by the vapor is recorded by noting the mercury levels in the side arm.

Equilibrium Vapor Pressure of a Liquid

Vapor molecules in equilibrium with a liquid in a closed system exert a pressure proportional to the vapor concentration. *The pressure exerted by a vapor in equilibrium with its corresponding liquid at a given temperature is called the* **equilibrium vapor pressure** *of the liquid.* Figure 12-11 shows the apparatus and method used to measure the equilibrium vapor pressure of a liquid.

Figure 12-12 is a graph of the equilibrium vapor pressures of water, diethyl ether, and ethanol. The curve shows that at any given temperature, vapor in equilibrium with liquid exerts a specific vapor pressure. The equilibrium vapor pressure of the liquid increases as temperature increases (although not in direct proportion).

Equilibrium Vapor Pressure and the Kinetic-Molecular Theory

The increase in equilibrium vapor pressure with increasing temperature can be explained in terms of the kinetic-molecular theory for the liquid and gaseous states. Increasing the temperature of a liquid

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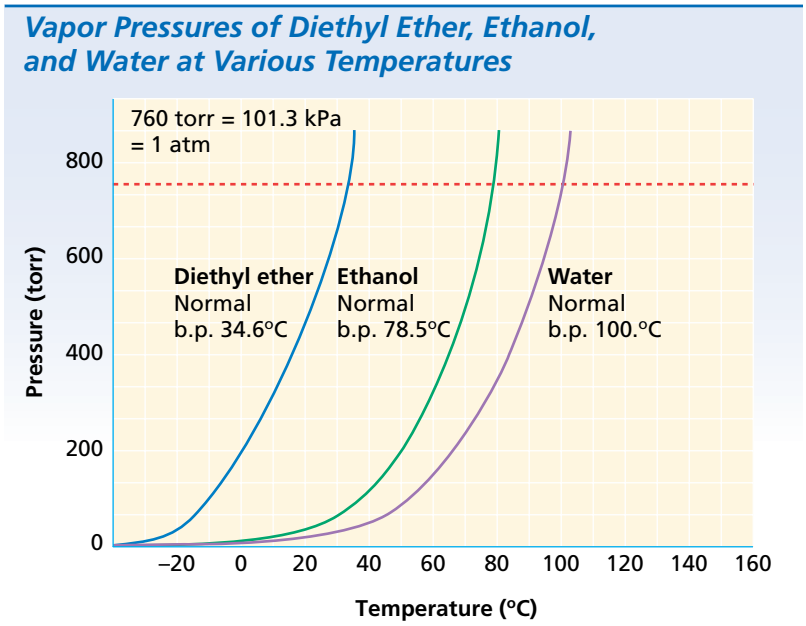

FIGURE 12-12 The vapor pressure of liquids increases as their temperature increases. A liquid boils when its vapor pressure equals the pressure of the atmosphere.

increases its average kinetic energy. That, in turn, increases the number of molecules that have enough energy to escape from the liquid phase into the vapor phase. The resulting increased evaporation rate increases the concentration of molecules in the vapor phase, which in turn increases the equilibrium vapor pressure. The liquid-vapor equilibrium is thus disturbed. However, the increase in concentration of vapor molecules then increases the rate at which molecules condense to liquid. Equilibrium is soon reestablished, but at a higher equilibrium vapor pressure.

Volatile and Nonvolatile Liquids

Because all liquids have characteristic forces of attraction between their particles, every liquid has a specific equilibrium vapor pressure at a given temperature. The stronger these attractive forces are, the smaller is the percentage of liquid particles that can evaporate at any given temperature. A low percentage of evaporation results in a low equilibrium vapor pressure. **Volatile liquids,** *which are liquids that evaporate readily,* have relatively weak forces of attraction between particles. Ether is a typical volatile liquid. Nonvolatile liquids, which evaporate slowly, have relatively strong attractive forces between particles. Molten ionic compounds are examples of nonvolatile liquids.

It is important not to confuse the equilibrium vapor pressure of a liquid with the pressure of a vapor not in equilibrium with its corresponding liquid. The equilibrium vapor pressure of a liquid depends only on temperature. The pressure of a vapor not in equilibrium with the corresponding liquid follows the gas laws, like any other gas. Its pressure is inversely proportional to its volume at constant temperature, according to Boyle's law.

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Boiling

Equilibrium vapor pressures can be used to explain and define the concept of boiling, which you read about in Section 12-1. **Boiling** *is the conversion of a liquid to a vapor within the liquid as well as at its surface. It occurs when the equilibrium vapor pressure of the liquid equals the atmospheric pressure.*

If the temperature of the liquid is increased, the equilibrium vapor pressure also increases. Finally, the boiling point is reached. *The* **boiling point** *of a liquid is the temperature at which the equilibrium vapor pressure of the liquid equals the atmospheric pressure.* The lower the atmospheric pressure is, the lower the boiling point is. Therefore, at high elevations, where atmospheric pressures are lower than at sea level, a cooking liquid boils at a lower temperature and foods take longer to cook.

At the boiling point, all of the heat absorbed goes to evaporate the liquid, and the temperature remains constant as long as the pressure does not change. If the pressure above the liquid being heated is increased, the temperature of the liquid will rise until the vapor pressure equals the new pressure and the liquid boils once again. This is the principle behind the operation of a pressure cooker. The cooker is sealed so that steam pressure builds up over the surface of the boiling water inside. The pressure increases the boiling temperature of the water, resulting in shorter cooking times. Conversely, a device called a vacuum evaporator causes boiling at lower-than-normal temperatures. Vacuum evaporators are used to remove water from milk and sugar solutions. Under reduced pressure, the water boils away at a temperature low enough to avoid scorching the milk or sugar. This process is used to prepare evaporated milk and sweetened condensed milk.

At normal atmospheric pressure (1 atm, 760. torr, or 101.3 kPa), the boiling point of water is exactly 100.°C. This temperature is known as the *normal* boiling point of water. The normal boiling points of water and other liquids are shown in Figure 12-12. Note that the normal boiling point of each liquid is the temperature at which the liquid's equilibrium vapor pressure equals 760 torr.

Energy and Boiling

As you know from experience, heat must be added continuously in order to keep a liquid boiling. A pot of boiling water stops boiling almost immediately after it is removed from the stove. Suppose you were to carefully measure the temperature of a boiling liquid and its vapor. You might be surprised to find that they are at the same constant temperature. The temperature, or average kinetic energy of the particles, at the boiling point remains constant despite the continuous addition of heat. Where does the added heat energy go? It is used to overcome the attractive forces between molecules of the liquid during the liquid-to-gas change. The energy is stored in the vapor as potential energy.

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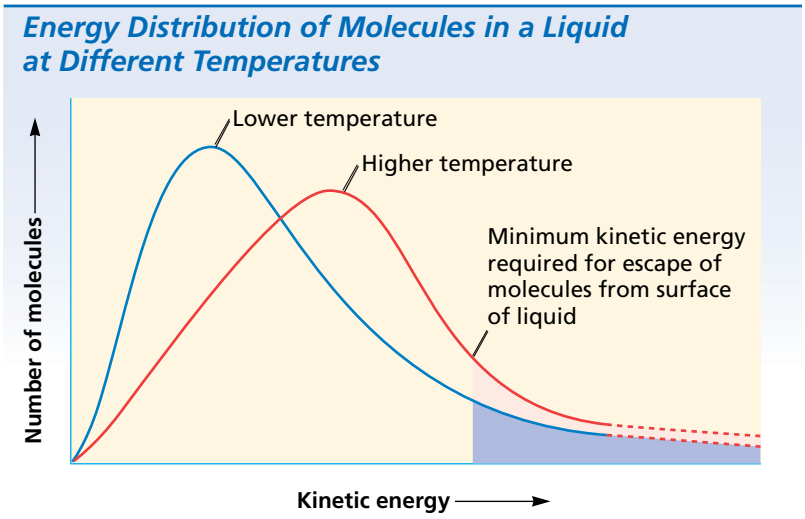
Energy Distribution of Molecules in a Liquid at Different Temperatures
Lower temperature
Higher temperature
Minimum kinetic energy required for escape of molecules from surface of liquid
Number of molecules
Kinetic energy

FIGURE 12-13 The number of molecules in a liquid with various kinetic energies is represented at two different temperatures. Notice the shaded area, which shows the minimum amount of kinetic energy required for evaporation to take place.

Molar Heat of Vaporization

The amount of heat energy needed to vaporize one mole of liquid at its boiling point is called the liquid's **molar heat of vaporization.** The magnitude of the molar heat of vaporization is a measure of the attraction between particles of the liquid. The stronger this attraction is, the more energy that is required to overcome it, which results in a higher molar heat of vaporization. Each liquid has a characteristic molar heat of vaporization. Compared with other liquids, water has an unusually high molar heat of vaporization due to the extensive hydrogen bonding in liquid water. This property makes water a very effective cooling agent. When water evaporates from your skin, the escaping molecules carry a great deal of heat away with them. Figure 12-13 shows the distribution of the kinetic energies of molecules in a liquid at two different temperatures. You can see that at the higher temperature a greater portion of the molecules have the kinetic energy required to escape from the liquid surface and become vapor.

Freezing and Melting

As you learned in Section 12-1, the physical change of a liquid to a solid is called freezing. Freezing involves a loss of heat energy by the liquid and can be represented by the following reaction.

$$\text{liquid} \longrightarrow \text{solid} + \text{heat energy}$$

In the case of a pure crystalline substance, this change occurs at constant temperature. *The normal* **freezing point** *is the temperature at which the solid and liquid are in equilibrium at 1 atm (760. torr, or 101.3 kPa) pressure.* At the freezing point, particles of the liquid and the solid have the same average kinetic energy. Therefore, the energy loss during freezing is

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a loss of potential energy that was present in the liquid. At the same time energy decreases, there is a significant increase in particle order because the solid state of a substance is much more ordered than the liquid state, even at the same temperature.

Melting, the reverse of freezing, also occurs at constant temperature. As a solid melts, it continuously absorbs heat, as represented by the following equation.

$$\text{solid} + \text{heat energy} \longrightarrow \text{liquid}$$

For pure crystalline solids, the melting point and freezing point are the same. At equilibrium, melting and freezing proceed at equal rates. The following general equilibrium equation can be used to represent these states.

$$\text{solid} + \text{heat energy} \rightleftharpoons \text{liquid}$$

At normal atmospheric pressure, the temperature of a system containing ice and liquid water will remain at 0.°C as long as both ice and water are present. That temperature will persist no matter what the surrounding temperature. As predicted by Le Châtelier's principle, adding heat to such a system shifts the equilibrium to the right. That shift increases the proportion of liquid water and decreases that of ice. Only after all the ice has melted will the addition of heat increase the temperature of the system.

Molar Heat of Fusion

The amount of heat energy required to melt one mole of solid at its melting point is its **molar heat of fusion.** The heat absorbed increases the potential energy of the solid as its particles are pulled apart, overcoming the attractive forces holding them together. At the same time, there is a significant decrease in particle order as the substance makes the transformation from solid to liquid. Similar to the molar heat of vaporization, the magnitude of the molar heat of fusion depends on the attraction between the solid particles.

Sublimation and Deposition

At sufficiently low temperature and pressure conditions, a liquid cannot exist. Under such conditions, a solid substance exists in equilibrium with its vapor instead of its liquid, as represented by the following equation.

$$\text{solid} + \text{heat energy} \rightleftharpoons \text{vapor}$$

The change of state from a solid directly to a gas is known as **sublimation.** The reverse process is called **deposition,** *the change of state from a gas directly to a solid.* Among the common substances that sublime at ordinary temperatures are dry ice (solid CO_2) and iodine. Ordinary ice sublimes slowly at temperatures lower than its melting point (0.°C). This explains how a thin layer of snow can eventually disappear, even if the temperature remains below 0.°C. Sublimation occurs in

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frost-free refrigerators when the temperature in the freezer compartment is periodically raised to cause any ice that has formed to sublime. A blower then removes the water vapor that has formed. The formation of frost on a cold surface is a familiar example of deposition.

Phase Diagrams

A **phase diagram** *is a graph of pressure versus temperature that shows the conditions under which the phases of a substance exist.* A phase diagram also reveals how the states of a system change with changing temperature or pressure.

Figure 12-14 shows the phase diagram for water over a range of temperatures and pressures. Note the three curves, AB, AC, and AD. Curve AB indicates the temperature and pressure conditions at which ice and water vapor can coexist at equilibrium. Curve AC indicates the temperature and pressure conditions at which liquid water and water vapor coexist at equilibrium. Similarly, curve AD indicates the temperature and pressure conditions at which ice and liquid water coexist at equilibrium. Because ice is less dense than liquid water, an increase in pressure lowers the melting point. (Most substances have a positive slope for this curve.) Point A is the triple point of water. *The* **triple point** *of a substance indicates the temperature and pressure conditions at which the solid, liquid, and vapor of the substance can coexist at equilibrium.* Point C is the critical point of water. *The* **critical point** *of a substance indicates the critical temperature and critical pressure. The* **critical temperature** *(t_c) is the temperature above which the substance cannot exist in the liquid state.* The critical temperature of water is 373.99°C. Above this temperature, water cannot be liquefied, no matter how much pressure is

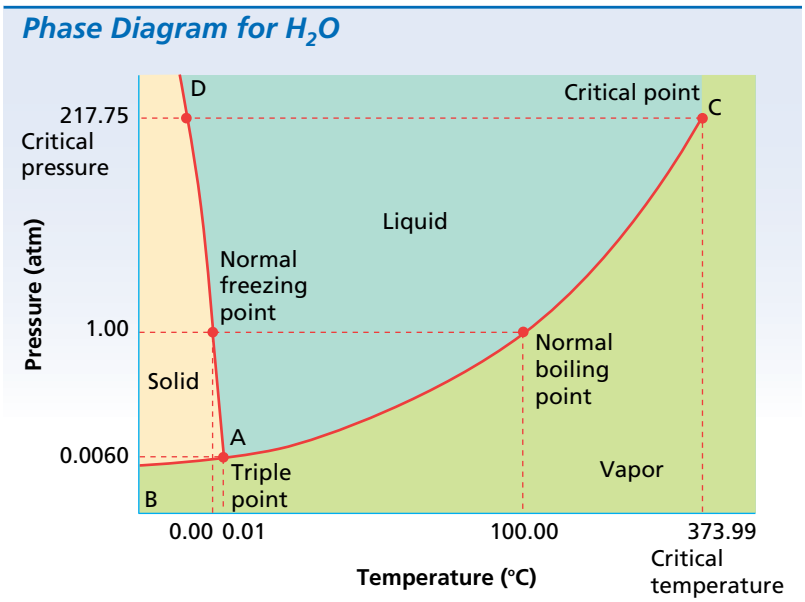

FIGURE 12-14 This phase diagram shows the relationships between the physical states of water and its pressure and temperature.

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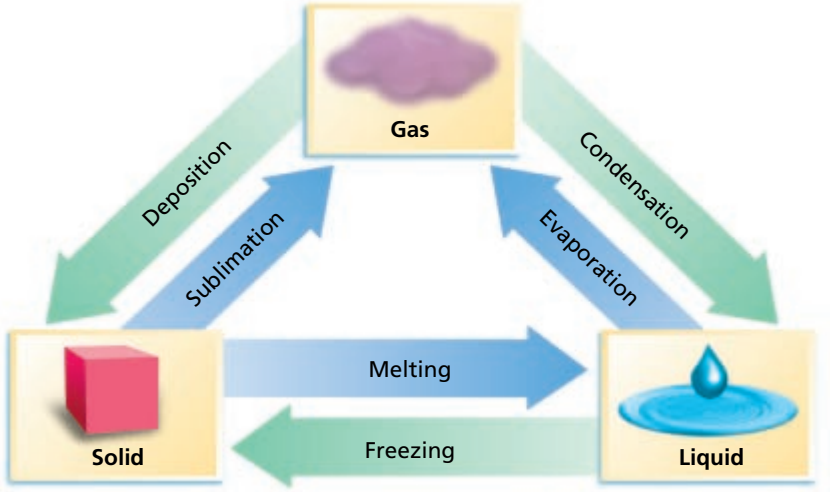
FIGURE 12-15 Solids, liquids, and gases can undergo various changes of state. The changes shown in green are exothermic, and those shown in blue are endothermic.



applied. *The* **critical pressure** *(P_c) is the lowest pressure at which the substance can exist as a liquid at the critical temperature. The critical pressure of water is 217.75 atm.*

The phase diagram in Figure 12-14 indicates the normal boiling point and the normal freezing point of water. It also shows how boiling point and freezing point change with pressure. As shown by the slope of line AD, ice melts at a higher temperature with decreasing pressure. Below the triple point, the temperature of sublimation decreases with decreasing pressure. Foods are freeze-dried by freezing the food and then lowering the pressure to cause the ice in the food to sublime rather than melt. Figure 12-15 summarizes the changes of state of solids, liquids, and gases.

SECTION REVIEW

1. What is equilibrium?
2. State Le Châtelier's principle.
3. What happens when a liquid-vapor system at equilibrium experiences an increase in temperature? What happens when it experiences a decrease in temperature?
4. What would be an example of deposition?
5. What is the equilibrium vapor pressure of a liquid?
6. What is the boiling point of a liquid?
7. In the phase diagram for water, what is meant by the triple point and the critical point?
8. Refer to the phase diagram for water on page 381 to answer the following questions.
   a. Describe all the phase changes a sample of solid water would undergo when heated to its critical temperature at a pressure of 1.00 atm.
   b. Describe all the phase changes a sample of water vapor would undergo when cooled to 5°C at a pressure of 1.00 atm.
   c. At approximately what pressure will water be a vapor at 0°C?
   d. Within what range of pressures will water be a liquid at temperatures above its normal boiling point?

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Phase-Change Materials

The real estate ad of tomorrow could read like this: "Just listed! Perfect starter home! Two bedrooms, 2 1/2 baths, walk-in closets, heats and cools itself with minimal electricity or other power." Ival Salyer, a senior research scientist at the University of Dayton Research Institute, says that homes like these may soon be commonplace. Phase-change technology will help control indoor temperature with walls that melt or freeze a bit as the weather changes.

When any material goes through a change in its physical form or state, it releases or absorbs heat. Salyer has designed walls that work on this principle. The wallboards are filled with a type of paraffin that melts or freezes above or below 75°F. When the temperature outside rises above 75°F, the paraffin melts and absorbs the heat inside the house. The opposite happens when the outdoor temperature drops. This change of state keeps the temperature of a house comfortably constant while using little power other than the heat of the sun.

By heating the material with electricity overnight, heat could be stored by changing the paraffin in the walls to a liquid state. When the heat is discontinued, the walls would freeze, radiating heat into the house and keeping it warm all day.

According to Salyer, because state change is an inherent property of matter, the walls heat and cool automatically, with no need for monitoring by people and no degradation from wear.

Changes of state are physical changes that can be exothermic or endothermic, depending on the direction of energy flow between an object and its surroundings.

Another recent discovery that can dramatically reduce building, heating, and cooling costs is the use of molded inserts of phase-change materials in the hollow spaces of hollow-core concrete blocks. In the outside walls of buildings, this phase-change material can store warmth from the winter sun for heating and the coolness of a summer night for cooling.

Salyer foresees this technology being used in dozens of other applications. Phase-change material is already being marketed as a food warmer; after being microwaved for a few minutes, a pillow-like pad can release heat for hours. The same idea is being adapted for use with bowls and plates to keep food warm. Winter weather might not feel quite so harsh with phase-change material lining coats, hats, and gloves. Phase-change flowerpots could keep plants warm, and the asphalt of highway bridges and liners for car batteries could be protected from freezing with the use of phase-change materials. Phase-change uniforms for firefighters and soldiers could keep them comfortably cool, and the material could be used as a protective, heat-resistant coating around airplane flight-data recorders.

1. *How does Ival Salyer think his research into phase-change materials will benefit society?*
2. *What benefits do you see for Mr. Salyer's research?*

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SECTION 12-4

Water

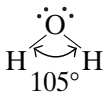
Objectives

- Describe the structure of a water molecule.
- Discuss the physical properties of water. Explain how they are determined by the structure of water.
- Calculate the amount of heat energy absorbed or released when a quantity of water changes state.

Water is a familiar substance in all three physical states: solid, liquid, and gas. On Earth, water is by far the most abundant liquid. Oceans, rivers, and lakes cover about 75% of Earth's surface. Significant quantities of water are also frozen in glaciers. Water is an essential component of all organisms; 70% to 90% of the mass of living things is water. The chemical reactions of most life processes take place in water, and water is frequently a reactant or product in such reactions. In order to better understand the importance of water, let us take a closer look at its structure and its properties.

Structure of Water

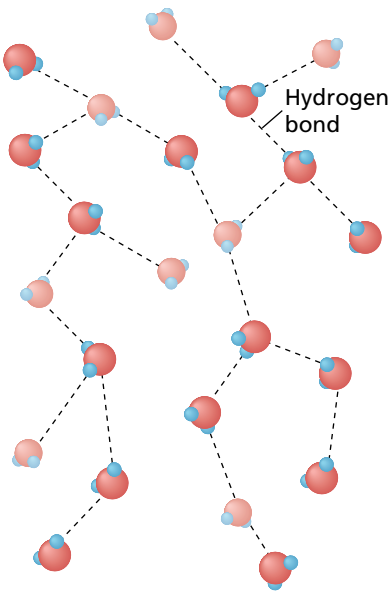
As discussed in Chapter 6, water molecules consist of two atoms of hydrogen and one atom of oxygen united by polar-covalent bonds. Research shows that a water molecule is bent. The structure can be represented as follows.



The angle between the two hydrogen-oxygen bonds is about 105°. This is close to the angle expected for sp^3 hybridization of the oxygen-atom orbitals.

The molecules in solid or liquid water are linked by hydrogen bonding. The number of linked molecules decreases with increasing temperature because increases in kinetic energy make hydrogen bond formation difficult. Nevertheless, there are usually from four to eight molecules per group in liquid water, as shown in Figure 12-16. If it were not for these molecular groups, water would be a gas at room temperature. Nonpolar molecules, such as methane, CH_4, that are similar in size and mass to water molecules, do not undergo hydrogen bonding. Such substances are gases at room temperature.

Ice consists of water molecules in the hexagonal arrangement shown in Figure 12-17. The empty spaces between molecules in this pattern account for the relatively low density of ice. As ice is heated, the increased energy of the molecules causes them to move and vibrate more vigorously. When the melting point is reached, the energy of the



Liquid water

FIGURE 12-16 The structure of liquid water shows that within the water molecule, oxygen and hydrogen are covalently bonded to each other, while the molecules are held together in groups by hydrogen bonds.

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molecules is so great that the rigid open structure of the ice crystals breaks down, and ice turns into liquid water.

Figures 12-16 and 12-17 also show that the hydrogen bonds between molecules of liquid water at 0.°C are fewer and more disordered than those between molecules of ice at the same temperature. Because the rigid open structure of ice has broken down, water molecules can crowd closer together. Thus, liquid water is denser than ice.

As the liquid water is warmed from 0.°C, the water molecules crowd still closer together. Water molecules are as tightly packed as possible at 3.98°C. At temperatures above 3.98°C, the increasing kinetic energy of the water molecules causes them to overcome molecular attractions. The molecules move farther apart as the temperature continues to rise. As the temperature approaches the boiling point, groups of liquid water molecules absorb enough energy to break up into separate molecules. Because of hydrogen bonding between water molecules, a high kinetic energy is needed, causing water's boiling point to be relatively high (100.°C) compared to other liquids that have similar molar masses.

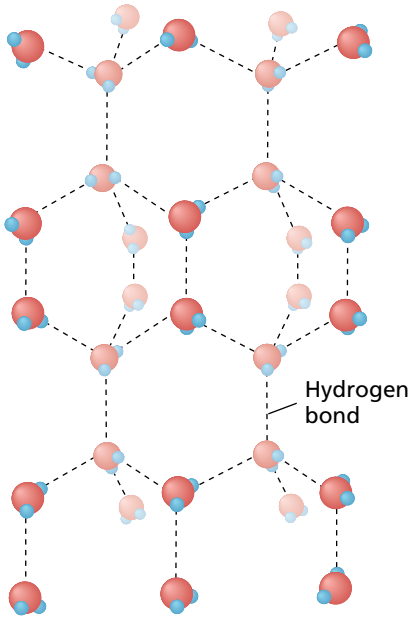

FIGURE 12-17 Ice contains the same types of bonding as liquid water. However, the structure of the hydrogen bonding is much more rigid and open than it is in liquid water.

Physical Properties of Water

At room temperature, pure liquid water is transparent, odorless, tasteless, and almost colorless. Any observable odor or taste is caused by impurities such as dissolved minerals, liquids, or gases.

As shown by its phase diagram in Figure 12-14 on page 381, water freezes at a pressure of 1 atm (101.3 kPa) and melts at 0.°C. The molar heat of fusion of ice is 6.009 kJ/mol. That value is relatively large compared with the molar heats of fusion of other solids. As you have read, water has the unusual property of expanding in volume as it freezes because its molecules form an open rigid structure. As a result, ice at 0.°C has a density of only about 0.917 g/cm^3, compared with a density of 0.999 84 g/cm^3 for liquid water at 0.°C.

This lower density explains why ice floats in liquid water. The insulating effect of floating ice is particularly important in the case of large bodies of water. If ice were more dense than liquid water, it would sink to the bottom of lakes and ponds, where it would be less likely to melt completely. The water of such bodies of water in temperate climates would eventually freeze solid, killing nearly all the living things in it.

Under a pressure of 1 atm (101.3 kPa), water boils at 100.°C. At this temperature, water's molar heat of vaporization is 40.79 kJ/mol. Both the boiling point and the molar heat of vaporization of water are quite high compared with those of nonpolar substances of comparable molecular mass, such as methane. The values are high because of the strong hydrogen bonding that must be overcome for boiling to occur. The high molar heat of vaporization makes water useful for household steam-heating systems. The steam (vaporized water) stores a great deal of heat. When the steam condenses in radiators, great quantities of heat are released.

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SAMPLE PROBLEM 12-1

How much heat energy is absorbed when 47.0 g of ice melts at STP? How much heat energy is absorbed when this same mass of liquid water boils?

SOLUTION

1 ANALYZE

Given: mass of $H_2O(s) = 47.0$ g
mass of $H_2O(l) = 47.0$ g
molar heat of fusion of ice = 6.009 kJ/mol (given on page 385)
molar heat of vaporization = 40.79 kJ/mol (given on page 385)

Unknown: heat energy absorbed when ice melts
heat energy absorbed when liquid water boils

2 PLAN

First, convert the mass of water in grams to moles.

$$\text{g } H_2O \times \frac{1 \text{ mol } H_2O}{\text{g } H_2O} = \text{mol } H_2O$$

Then, use the molar heat of fusion of a solid to calculate the amount of heat absorbed when the solid melts. Multiply the number of moles by the amount of energy needed to melt one mole of ice at its melting point (the molar heat of fusion of ice). Using the same method, calculate the amount of heat absorbed when water boils by using the molar heat of vaporization.

amount of substance (mol) × molar heat of fusion or vaporization (kJ/mol) = heat energy (kJ)

3 COMPUTE

$$47.0 \cancel{\text{g}}\ H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \cancel{\text{g}}\ H_2O} = 2.61 \text{ mol } H_2O$$

$$2.61 \cancel{\text{mol}} \times 6.009 \text{ kJ/}\cancel{\text{mol}} = 15.7 \text{ kJ (on melting)}$$

$$2.61 \cancel{\text{mol}} \times 40.79 \text{ kJ/}\cancel{\text{mol}} = 106 \text{ kJ (on vaporizing or boiling)}$$

4 EVALUATE

Units have canceled correctly. The answers have the proper number of significant digits and are reasonably close to estimated values of 18 (3 × 6) and 120 (3 × 40), respectively.

PRACTICE

1. What quantity of heat energy is released when 506 g of liquid water freezes? *Answer* 169 kJ
2. What mass of steam is required to release 4.97×10^5 kJ of heat energy on condensation? *Answer* 2.19×10^5 g

SECTION REVIEW

1. Why is a water molecule polar?
2. How is the structure of water responsible for some of water's unique characteristics?
3. Describe the arrangement of molecules in liquid water and in ice.
4. Why does ice float? Why is this phenomenon important?

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CHAPTER 12 REVIEW

CHAPTER SUMMARY

12-1

- The particles of a liquid are closer together and more ordered than those of a gas and less ordered than those of a solid.
- Liquids have a definite volume and a fairly high density, and they are relatively incompressible. Like gases, liquids can flow and are thus considered to be fluids. Liquids can dissolve other substances.
- Liquids have the ability to diffuse. They exhibit surface tension, and they can evaporate or boil. A liquid is said to freeze when it becomes a solid.

Vocabulary

capillary action (365)
evaporation (365)
fluid (363)
freezing (366)
surface tension (365)
vaporization (365)

12-2

- The particles of a solid are not nearly so free to move about as are those of a liquid or a gas. They can only vibrate about definite, fixed positions.
- Solids have a definite shape and may be crystalline or amorphous. They have a definite volume and are generally nonfluid. Additional characteristics of solids are high density, incompressibility, extremely low rates of diffusion, and definite melting points (for crystals).
- A crystal structure is the total three-dimensional array of points that describes the arrangement of the particles of a crystal. A crystal can be classified into one of seven crystalline systems on the basis of the three-dimensional shape of its unit cell. A crystal can also be described as one of four types, based on the kind of particles it contains and the type of chemical bonding between its particles.
- Amorphous solids do not have a regular shape. Instead, they take on whatever shape is imposed on them.

Vocabulary

amorphous solids (368)
crystal (368)
crystal structure (369)
crystalline solids (368)
melting (368)
melting point (368)
supercooled liquids (368)
unit cell (369)

12-3

- A liquid in a closed system will gradually reach a liquid-vapor equilibrium as the rate at which molecules condense equals the rate at which they evaporate.
- When two opposing changes occur at equal rates in the same closed system, the system is said to be in dynamic equilibrium. Le Châtelier's principle states that if any factor determining an equilibrium is changed, the system will adjust itself in a way that tends to minimize that change.
- The pressure exerted by a vapor in equilibrium with its corresponding liquid at a given temperature is the liquid's equilibrium vapor pressure. A liquid boils when the equilibrium vapor pressure of the liquid is equal to the atmospheric pressure. The amount of heat energy required to vaporize one mole of liquid at its boiling point is called the molar heat of vaporization.
- Freezing involves a loss of energy, in the form of heat, by a liquid. Melting is the physical change of a solid to a liquid by the addition of heat. The amount of heat required to melt one mole of solid at its melting point is its molar heat of fusion.

Vocabulary

boiling (378)
boiling point (378)
condensation (373)
critical point (381)
critical pressure (382)
critical temperature (381)
deposition (380)
equilibrium (372)
equilibrium vapor pressure (376)
freezing point (379)
Le Châtelier's principle (374)
molar heat of fusion (380)
molar heat of vaporization (379)
phase (373)
phase diagram (381)
sublimation (380)
triple point (381)
volatile liquids (377)

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CHAPTER SUMMARY continued

12-4

- Water is a polar-covalent compound. A water molecule has a bent shape and a partial negative charge near its oxygen atom and a partial positive charge near each hydrogen atom.
- The structure and the types of bonds water is able to form are responsible for its relatively high melting point, molar heat of fusion, boiling point, and molar heat of vaporization.
- The structure and bonding of water also explain why water expands upon freezing and why ice is able to float in liquid water.

REVIEWING CONCEPTS

1. What is a fluid? (12-1)
2. What is surface tension? (12-1)
3. Give two reasons why evaporation is a crucial process in nature. (12-1)
4. List seven properties of solids, and explain each in terms of the kinetic-molecular theory of solids. (12-2)
5. a. List four common examples of amorphous solids.
   b. Why is glass sometimes classified as a supercooled liquid?
   c. Name some uses of glass. (12-2)
6. Distinguish between a crystal structure, a lattice, and a unit cell. (12-2)
7. a. List and describe the four types of crystals in terms of the nature of their component particles and the type of bonding between them.
   b. What physical properties are associated with each type of crystal? (12-2)
8. Using Figure 12-12, estimate the approximate equilibrium vapor pressure of each of the following at the specified temperature.
   a. water at 40°C
   b. water at 80°C
   c. diethyl ether at 20°C
   d. ethanol at 60°C (12-3)
9. a. What is sublimation?
   b. Give two examples of common substances that sublime at ordinary temperatures. (12-3)
10. What is meant by the normal freezing point of a substance? (12-3)
11. Explain why the vapor pressure of a liquid increases with increasing temperature. (12-3)
12. Explain how the attractive forces between the particles in a liquid and the equilibrium vapor pressure of that liquid are related. (12-3)
13. a. Explain the relationship between atmospheric pressure and the actual boiling point of a liquid.
    b. During continual boiling at this pressure, what is the relationship between the temperature of the liquid and that of its vapor?
    c. How can this phenomenon be explained? (12-3)
14. Explain the relationship between the magnitude of the molar heat of vaporization of a liquid and the strength of attraction between the particles of that liquid. (12-3)
15. Explain the relationship between the molar heat of fusion of a solid and the strength of attraction between its particles. (12-3)
16. Describe the structure of a water molecule. (12-4)
17. List at least eight physical properties of water. (12-4)

PROBLEMS

Molar Heat

18. a. The molar heat of vaporization for water is 40.79 kJ/mol. Express this heat of vaporization in joules per gram.
    b. The molar heat of fusion for water is 6.009 kJ/mol. Express this heat of fusion in joules per gram.
19. The standard molar heat of vaporization for water is 40.79 kJ/mol. How much energy would be required to vaporize each of the following?
    a. 5.00 mol H_2O
    b. 45.0 g H_2O
    c. 8.45×10^{10} molecules H_2O

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20. The molar heat of fusion for water is 6.009 kJ/mol. How much energy would be required to melt each of the following?
a. 12.75 mol ice b. 6.48×10^5 kg ice

21. Calculate the molar heat of vaporization of a substance given that 0.433 mol of the substance absorbs 36.5 kJ of energy when it is vaporized.

22. Given that a substance has a molar mass of 259.0 g/mol and a 71.8 g sample of the substance absorbs 4.307 kJ when it melts,
a. calculate the number of moles in the sample.
b. calculate the molar heat of fusion.

23. a. Calculate the number of moles in a liquid sample of a substance that has a molar heat of fusion of 3.811 kJ/mol, given that the sample releases 83.2 kJ when it freezes.
b. Calculate the molar mass of this substance if the mass of the sample is 5519 g.

Water

24. Which contains more molecules of water; 5.00 cm^3 of ice at 0°C or 5.00 cm^3 of liquid water at 0.°C? How many more? What is the ratio of the numbers of molecules in these two samples?

25. Which contains more molecules of water (density = 4.87×10^{-6} g/cm^3); 5.00 cm^3 of liquid water at 0.°C or 5.00 cm^3 of water vapor at STP? How many more? What is the ratio of the numbers of molecules in these two samples?

26. a. What volume and mass of steam at 100.°C and 1.00 atm would, during condensation, release the same amount of heat as 100. cm^3 of liquid water during freezing?
b. What do you note, qualitatively, about the relative volumes and masses of steam and liquid water required to release the same amount of heat? (Hint: See Sample Problem 12-1.)

MIXED REVIEW

27. Find the molar heat of vaporization for a substance, given that 3.21 mol of the substance absorbs 28.4 kJ of energy when it changes from a liquid to a gas.

28. Water's molar heat of fusion is 6.009 kJ/mol. Calculate the amount of energy required to melt 7.95×10^5 g of ice.

29. A certain substance has a molar heat of vaporization of 31.6 kJ/mol. How much of the substance is in a sample that requires 57.0 kJ to vaporize?

30. Given that water has a molar heat of vaporization of 40.79 kJ/mol, how many grams of water could be vaporized by 0.545 kJ?

31. Calculate the amount of energy released by the freezing of 13.3 g of a liquid substance, given that the substance has a molar mass of 82.9 g/mol and a molar heat of fusion of 4.60 kJ/mol.

32. What volume and mass of steam at 100.°C and 760. torr would release the same amount of heat during condensation as 65.5 cm^3 of liquid water would release during freezing?

33. A substance has a molar heat of fusion of 3.43 kJ/mol. Calculate the molar mass of the substance, given that a 64.2 g sample of it absorbs 2.77 kJ on melting.

34. The following liquid-vapor system is at equilibrium at a given temperature in a closed system.

$$\text{liquid} + \text{heat energy} \rightleftharpoons \text{vapor}$$

Suppose the temperature is increased and equilibrium is established at the higher temperature. How does the final value of each of the following compare with its initial value? (In each case, answer either higher, lower, or the same.)
a. the rate of evaporation
b. the rate of condensation
c. the final concentration of vapor molecules
d. the final number of liquid molecules

35. Decide whether the temperature of a liquid-vapor equilibrium system should be increased or decreased to make each of the following changes in the system.
a. an increased final rate of evaporation
b. an increased final concentration of vapor
c. an increased final rate of condensation
d. an increased final number of liquid molecules.

36. Given a sample of water at any point on curve AB in Figure 12-14, what effect would each of the following changes have on that sample?
a. adding heat energy at constant pressure
b. decreasing the volume at constant temperature
c. removing heat energy at constant pressure
d. increasing the volume at constant temperature

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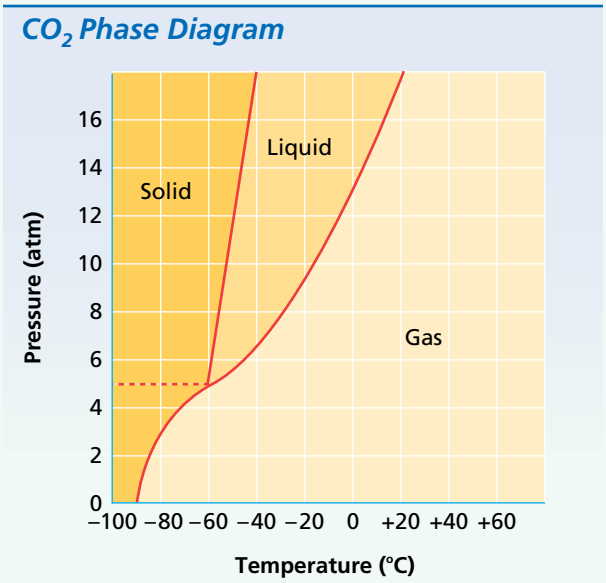
37. Using the phase diagram for CO_2, describe all the phase changes that would occur when CO_2 is heated from –100°C to –10°C at a constant pressure of 6 atm.



CRITICAL THINKING

38. Applying Ideas Explain the role of humidity of the air in determining relative comfort on a hot day.

39. Interpreting Concepts During the freezing of a substance, energy is being removed from that substance. Yet the temperature of the liquid-solid system remains constant. Explain this phenomenon.

40. Applying Models At normal atmospheric pressure, the temperature of an ice-water system remains at 0°C as long as both ice and liquid water are present, regardless of the surrounding temperature. Explain this in terms of Le Châtelier's principle.

41. Describe the forces that must be overcome to explain why the heat of vaporization of a substance is always greater than its heat of fusion.

42. Predicting Outcomes Given a sample of water at any point on curve AD in Figure 12-14, how could more of the liquid water in that sample be converted into a solid without changing the temperature? Explain your reasoning.

43. Interpreting Diagrams Refer to the phase diagram in question 37.

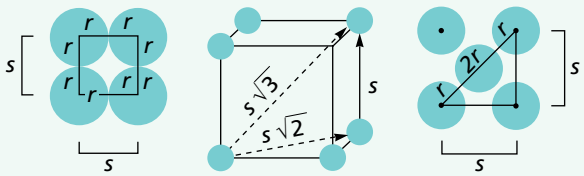
a. Explain what happens when solid CO_2 ("dry ice") warms up to room temperature at normal atmospheric pressure.

b. Is there a pressure below which liquid CO_2 cannot exist? Estimate that pressure from the graph.

44. Interpreting Concepts Methane, CH_4, which is similar to water in molecular size and mass, is a gas at room temperature. However, water is a liquid at that temperature. Explain why.

45. Three simple unit cells found in metals are shown below. The dimensions of each unit cell can be described mathematically using the following information.

s = length of the edge
r = atomic radius



Which of the following relationships applies to the simple cubic cell?

a. $2r = s$
b. $8r = 2s$
c. $r = s$
d. $2s = r$

46. Which of the following relationships applies to the face-centered cubic cell?

a. $2s = 4r$
b. $2r = s$
c. $4r = s\sqrt{2}$
d. $3r = s$

TECHNOLOGY & LEARNING

47. Graphing Calculator Calculating Vapor Pressure Using a Table

The graphing calculator can run a program that calculates a table for the vapor pressure in atmospheres at different temperatures (K) given the number of moles of a gas and its volume (V). Given a 0.50 mol gas sample with a volume of 10 L, you can calculate the pres-

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sure at 290 K, using a table. Use this program to create the table. Next, use the table to perform the calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

Note: All answers show five significant digits.

a. What is the pressure for a gas with a mass of 1.3 mol, volume of 8.0 L, and temperature of 320° K?
b. What is the pressure for a gas with a mass of 1.5 mol, volume of 10.0 L, and temperature of 340° K?
c. Two gases are measures at 300° K. One has a mass of 1.3 mol and has a volume of 7.5 L, and the other has a mass of 0.5 mol and a volume of 10.0 L. Which gas has the lesser pressure?

HANDBOOK SEARCH

48. The *Elements Handbook* contains a table of properties for each group that includes information on the crystal structures of the elements. Most metals crystallize in one of three lattice arrangements: body-centered cubic, face-centered cubic, or hexagonal close-packed. Figure 12-7 shows a model of the face-centered cubic lattice for sodium chloride. Use this figure and the information in the *Elements Handbook* to answer the following.

a. What elements in Group 2 have the same lattice structure as sodium chloride?
b. How would the model of an element in a face-centered cubic lattice differ from the compound shown in Figure 12-7?
c. The body-centered cubic lattice is the least-efficient packing structure of the metals. What elements in Groups 1 and 2 show this arrangement?

RESEARCH & WRITING

49. Ceramics are formed from silicates found in the soil. Artists use them to create pottery, but engineers and scientists have created ceramics with superconductive properties. Investigate the growing field of superconductive ceramics.

50. Liquid crystals are substances that possess the combined properties of both liquids and crystals. Write a report on these substances and the various uses we are finding for them.

51. Consult reference materials at the library, and prepare a report on the process of freeze-drying, describing its history and applications.

52. Prepare a report about the adjustments that must be made when cooking and baking at high elevations. Collect instructions for high-elevation adjustments from packages of prepared food mixes. Explain why changes must be made in recipes that will be prepared at high elevations. Check your library for cookbooks containing information about food preparation at high elevations.

ALTERNATIVE ASSESSMENT

53. Compile separate lists of crystalline and amorphous solids found in your home. Compare your lists with those of your classmates.

54. Design an experiment to grow crystals of various safe, common household materials. Record the conditions under which each type of crystal is best grown.

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CHAPTER 13

Solutions

Solutions are homogeneous mixtures of two or more substances in a single phase.

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Types of Mixtures

SECTION 13-1

Objectives

- Distinguish between heterogeneous and homogeneous mixtures.
- List three different solute-solvent combinations.
- Compare the properties of suspensions, colloids, and solutions.
- Distinguish between electrolytes and nonelectrolytes.

It is easy to determine that some materials are mixtures because you can see their component parts. For example, soil is a mixture of various substances, including small rocks and decomposed animal and plant matter. You can see this by picking up some soil in your hand and looking at it closely. Milk, on the other hand, does not appear to be a mixture, but in fact it is. Milk is composed principally of fats, proteins, milk sugar, and water. If you look at milk under a microscope, it will look something like Figure 13-1(a). You can see round lipid droplets that measure from 1 to 10 µm in diameter. Irregularly shaped protein (casein) particles that are about 0.2 µm wide can also be seen. Both milk and soil are examples of heterogeneous mixtures because their composition is not uniform.

Salt (sodium chloride) and water form a homogeneous mixture. The sodium and chloride ions are interspersed among the water molecules, and the mixture appears uniform throughout. A model for a homogeneous mixture like salt water is shown in Figure 13-1(b).

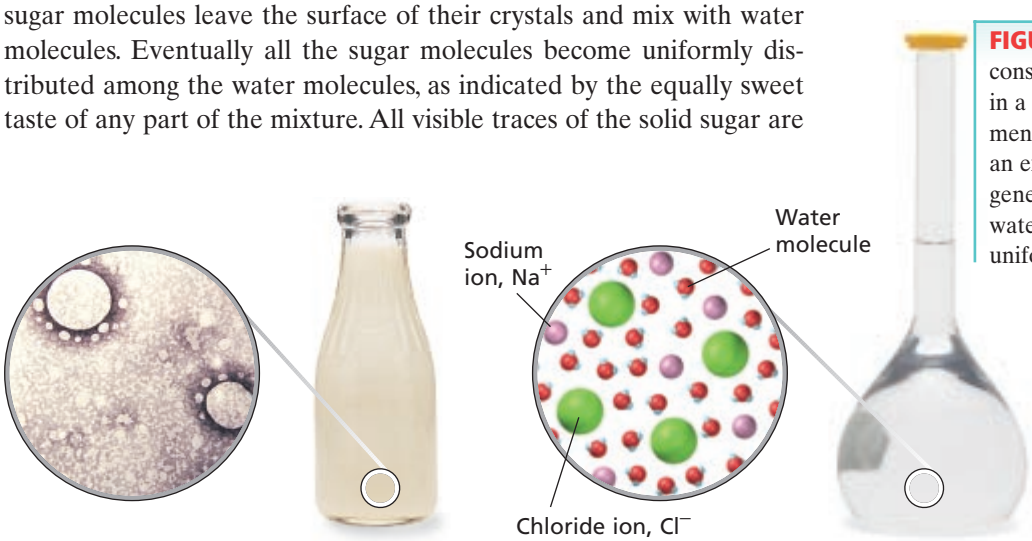
CHEMISTRY INTERACTIVE TUTOR

Module 1: States of Matter/Classes of Matter

Solutions

Suppose a sugar cube is dropped into a glass of water. You know from experience that the sugar will dissolve. Sugar is described as "soluble in water." *By* **soluble** *we mean capable of being dissolved.*

What happens as sugar dissolves? The lump gradually disappears as sugar molecules leave the surface of their crystals and mix with water molecules. Eventually all the sugar molecules become uniformly distributed among the water molecules, as indicated by the equally sweet taste of any part of the mixture. All visible traces of the solid sugar are



(a) Heterogeneous mixture—milk

(b) Homogeneous mixture—saltwater solution

FIGURE 13-1 (a) Milk consists of visible particles in a nonuniform arrangement. (b) Salt water is an example of a homogeneous mixture. Ions and water molecules are in a uniform arrangement.

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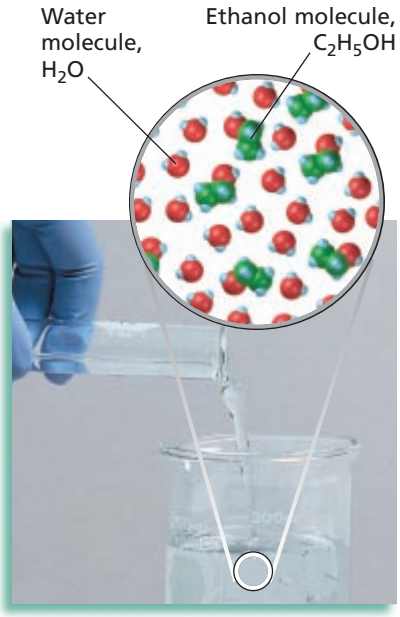
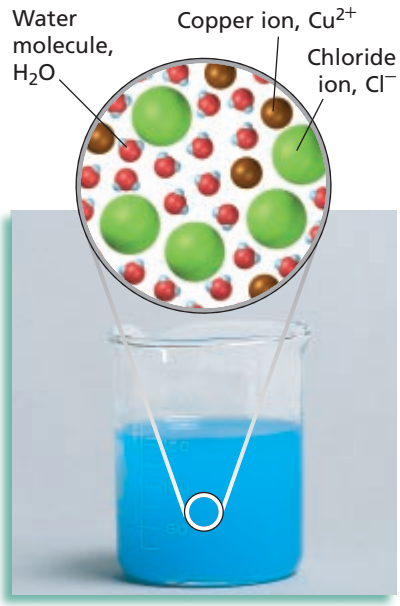


(a)



(b)

FIGURE 13-2 The solute in a solution can be a solid, liquid, or gas. (a) The ethanol-water solution is made from a liquid solute in a liquid solvent. (b) The copper(II) chloride–water solution is made from a solid solute in a liquid solvent. Note that the composition of each solution is uniform.

gone. Such a mixture is called a solution. *A* **solution** *is a homogeneous mixture of two or more substances in a single phase*. In a solution, atoms, molecules, or ions are thoroughly mixed, resulting in a mixture that has the same composition and properties throughout.

Components of Solutions

In the simplest type of solution, such as a sugar-water solution, the particles of one substance are randomly mixed with the particles of another substance. *The dissolving medium in a solution is called the* **solvent,** *and the substance dissolved in a solution is called the* **solute.** The solute is generally designated as that component of a solution that is of lesser quantity. In the ethanol-water solution shown in Figure 13-2, ethanol is the solute and water is the solvent. Occasionally, these terms have little meaning. For example, in a 50%-50% solution of ethanol and water, it would be difficult, and in fact unnecessary, to say which is the solvent and which is the solute.

In a solution, the dissolved solute particles are so small that they cannot be seen. They remain mixed with the solvent indefinitely, so long as the existing conditions remain unchanged. If the solutions in Figure 13-2 are poured through filter paper, both the solute and the solvent will pass through the paper. The solute-particle dimensions are those of atoms, molecules, and ions—which range from about 0.01 to 1 nm in diameter.

Types of Solutions

Solutions may exist as gases, liquids, or solids. Some possible solute-solvent combinations of gases, liquids, and solids in solutions are summarized in Table 13-1. In each example, one component is designated as the solvent and one as the solute.

Many alloys, such as brass (made from zinc and copper) and sterling silver (made from silver and copper), are solid solutions in which the atoms of two or more metals are uniformly mixed. By properly choosing the proportions of each metal in the alloy, many desirable properties

TABLE 13-1 ***Some Solute-Solvent Combinations for Solutions***

Solute state	Solvent state	Example
Gas	gas	oxygen in nitrogen
Gas	liquid	carbon dioxide in water
Liquid	gas	water in air
Liquid	liquid	alcohol in water
Liquid	solid	mercury in silver and tin (dental amalgam)
Solid	liquid	sugar in water
Solid	solid	copper in nickel (Monel™ alloy)

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(a) 24 karat **(b)** 14 karat

FIGURE 13-3 (a) 24-karat gold is pure gold. (b) 14-karat gold is an alloy of gold and silver. 14-karat gold is 14/24, or 58.3%, gold.

can be obtained. For example, alloys can have higher strength and greater resistance to corrosion than the pure metals. Pure gold (24K), for instance, is too soft to use in jewelry. Alloying it with silver greatly increases its strength and hardness while retaining its appearance and corrosion resistance. Figure 13-3 shows a model for comparing pure gold with a gold alloy.

Suspensions

If the particles in a solvent are so large that they settle out unless the mixture is constantly stirred or agitated, the mixture is called a **suspension.** Think of a jar of muddy water. If left undisturbed, particles of soil collect on the bottom of the jar. The soil particles are much larger and denser than water molecules. Gravity pulls them to the bottom of the container. Particles over 1000 nm in diameter—1000 times as large as atoms, molecules, or ions—form suspensions. The particles in suspension can be separated from the heterogeneous mixtures by passing the mixture through a filter.

Colloids

Particles that are intermediate in size between those in solutions and suspensions form mixtures known as colloidal dispersions, or simply **colloids.** Particles between 1 nm and 1000 nm in diameter may form colloids. After large soil particles settle out of muddy water, the water is often still cloudy because colloidal particles remain dispersed in the water. If the cloudy mixture is poured through a filter, the colloidal particles will pass through, and the mixture will remain cloudy. The particles in a colloid are small enough to be suspended throughout the solvent by the constant movement of the surrounding molecules. The colloidal particles make up the *dispersed phase,* and water is the *dispersing medium*. Examples of the various types of colloids are given in Table 13-2. Note that some familiar terms, such as *emulsion* and *foam,* refer to specific types of colloids. For example, mayonnaise is an emulsion

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TABLE 13-2 *Classes of Colloids*

Class of colloid	Phases	Example
Sol	solid dispersed in liquid	paints, mud
Gel	solid network extending throughout liquid	gelatin
Liquid emulsion	liquid dispersed in a liquid	milk, mayonnaise
Foam	gas dispersed in liquid	shaving cream, whipped cream
Solid aerosol	solid dispersed in gas	smoke, airborne particulate matter, auto exhaust
Liquid aerosol	liquid dispersed in gas	fog, mist, clouds, aerosol spray
Solid emulsion	liquid dispersed in solid	cheese, butter

of oil droplets in water; the egg yolk in it acts as an emulsifying agent, which helps to keep the oil droplets dispersed.

FIGURE 13-4 A beam of light distinguishes a colloid from a solution. The particles in a colloid will scatter light, making the beam visible. The mixture of gelatin and water in the jar on the right is a colloid. The mixture of water and sodium chloride in the jar on the left is a true solution.

Tyndall Effect

Many colloids appear homogeneous because the individual particles cannot be seen. The particles are, however, large enough to scatter light. You have probably noticed that a headlight beam is visible on a foggy night. This effect, known as the Tyndall effect, occurs when light is scattered by colloidal particles dispersed in a transparent medium. The Tyndall effect is a property that can be used to distinguish between a solution and a colloid, as demonstrated in Figure 13-4.

The distinctive properties of solutions, colloids, and suspensions are summarized in Table 13-3. The individual particles of a colloid can be detected under a microscope if a bright light is cast on the specimen at a right angle. The particles, which appear as tiny specks of light, are seen to move rapidly in a random motion. This motion is due to collisions of rapidly moving molecules and is called Brownian motion, after its discoverer, Robert Brown.

TABLE 13-3 *Properties of Solutions, Colloids, and Suspensions*

Solutions	Colloids	Suspensions
Homogeneous	Heterogeneous	Heterogeneous
Particle size: 0.01–1 nm; can be atoms, ions, molecules	Particle size: 1–1000 nm, dispersed; can be aggregates or large molecules	Particle size: over 1000 nm, suspended; can be large particles or aggregates
Do not separate on standing	Do not separate on standing	Particles settle out
Cannot be separated by filtration	Cannot be separated by filtration	Can be separated by filtration
Do not scatter light	Scatter light (Tyndall effect)	May scatter light, but are not transparent

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Quick LAB

Observing Solutions, Suspensions, and Colloids

Wear Safety Goggles and an Apron.

Materials

- balance
- 7 beakers, 400 mL
- clay
- cooking oil
- flashlight
- gelatin, plain
- hot plate (to boil H_2O)
- red food coloring
- sodium borate ($Na_2B_4O_7 \cdot 10H_2O$)
- soluble starch
- stirring rod
- sucrose
- test-tube rack
- water

Procedure

1. Prepare seven mixtures, each containing 250 mL of water and one of the following substances.
   - **a.** 12 g of sucrose
   - **b.** 3 g of soluble starch
   - **c.** 5 g of clay
   - **d.** 2 mL of food coloring
   - **e.** 2 g of sodium borate
   - **f.** 50 mL of cooking oil
   - **g.** 3 g of gelatin

   Making the gelatin mixture: Soften the gelatin in 65 mL of cold water, and then add 185 mL of boiling water.
2. Observe the seven mixtures and their characteristics. Record the appearance of each mixture after stirring.
3. Transfer to individual test tubes 10 mL of each mixture that does not separate after stirring. Shine a flashlight on each mixture in a dark room. Make note of the mixtures in which the path of the light beam is visible.

Discussion

1. Using your observations, classify each mixture as a solution, suspension, or colloid.
2. What characteristics did you use to classify each mixture?

Solutes: Electrolytes vs. Nonelectrolytes

Substances that dissolve in water are classified according to whether they yield molecules or ions in solution. When an ionic compound dissolves, the positive and negative ions separate from each other and are surrounded by water molecules. These solute ions are free to move, making it possible for an electric current to pass through the solution. *A substance that dissolves in water to give a solution that conducts electric current is called an* **electrolyte.** Sodium chloride, NaCl, is an electrolyte, as is any soluble ionic compound. Certain highly polar molecular compounds, such as hydrogen chloride, HCl, are also electrolytes because HCl molecules form the ions H_3O^+ and Cl^- when dissolved in water.

By contrast, a solution containing neutral solute molecules does not conduct electric current because it does not contain mobile charged

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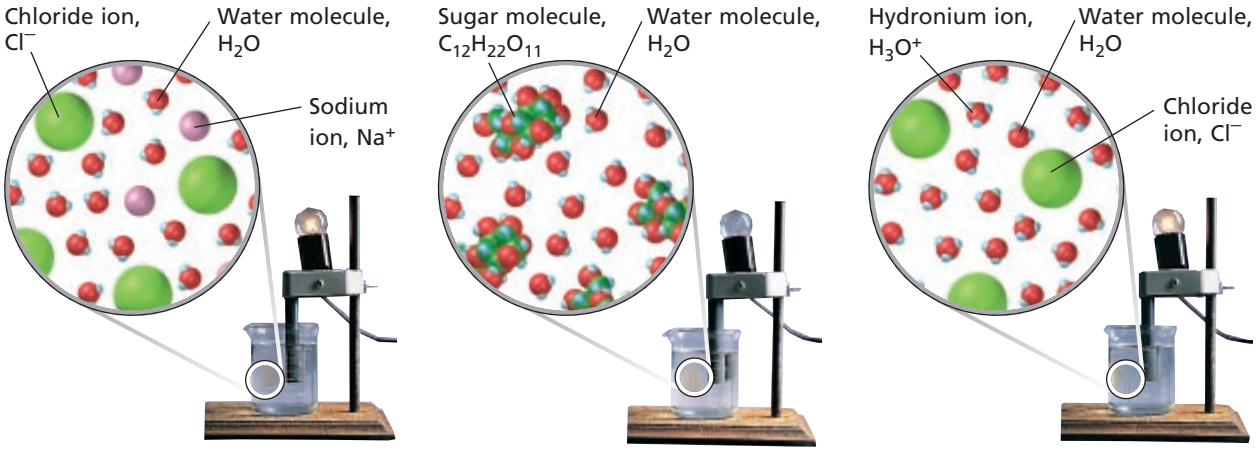

(a) Salt solution—electrolyte solute

(b) Sugar solution—nonelectrolyte solute

(c) Hydrochloric acid solution—electrolyte solute

FIGURE 13-5 (a) Sodium chloride dissolves in water to produce a salt solution that conducts electric current. NaCl is an electrolyte. (b) Sucrose dissolves in water to produce a sugar solution that does not conduct electricity. Sucrose is a nonelectrolyte. (c) Hydrogen chloride dissolves in water to produce a solution that conducts current. HCl is an electrolyte.

particles. *A substance that dissolves in water to give a solution that does not conduct an electric current is called a* **nonelectrolyte.** Sugar is a nonelectrolyte. Figure 13-5 shows an apparatus for testing the conductivity of solutions. The electrodes are conductors that are attached to a power supply and that make electric contact with the test solution. For a current to pass through the light-bulb filament, the test solution must provide a conducting path between the two electrodes. A nonconducting solution is like an open switch between the electrodes, and there is no current in the circuit.

The light bulb glows brightly if a solution that is a good conductor is tested. Such solutions contain solutes that are electrolytes. For a moderately conductive solution, however, the light bulb is dim. If a solution is a poor conductor, the light bulb does not glow at all. Such solutions contain solutes that are nonelectrolytes. You will learn more about the strengths and behavior of electrolytes in Chapter 14.

SECTION REVIEW

1. Classify the following as either a heterogeneous or homogeneous mixture, and explain your answers.
   a. orange juice b. tap water
2. a. What are substances called whose water solutions conduct electricity? b. Why does a saltwater solution conduct electricity? c. Why does a sugar-water solution not conduct electricity?
3. Make a drawing of the particles in an NaCl solution to show why this solution conducts electricity. Make a drawing of the particles in an NaCl crystal to show why pure salt does not conduct.
4. Describe one way to prove that a mixture of sugar and water is a solution and that a mixture of sand and water is not a solution.
5. Label the solute and solvent in each of the following:
   a. 14-karat gold
   b. water vapor in air
   c. carbonated, or sparkling, water
   d. hot tea

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The Solution Process

SECTION 13-2

Objectives

- List and explain three factors that affect the rate at which a solid solute dissolves in a liquid solvent.
- Explain solution equilibrium, and distinguish among saturated, unsaturated, and supersaturated solutions.
- Explain the meaning of "like dissolves like" in terms of polar and nonpolar substances.
- List the three interactions that contribute to the heat of solution, and explain what causes dissolution to be exothermic or endothermic.
- Compare the effects of temperature and pressure on solubility.

Factors Affecting the Rate of Dissolution

If you have ever tried to dissolve sugar in iced tea, you know that temperature has something to do with how quickly a solute dissolves. What other factors affect how quickly you can dissolve sugar in iced tea?

Increasing the Surface Area of the Solute

Sugar dissolves as sugar molecules leave the crystal surface and mix with water molecules. The same is true for any solid solute in a liquid solvent: molecules or ions of the solute are attracted by the solvent.

Because the dissolution process occurs at the surface of the solute, it can be speeded up if the surface area of the solute is increased. Crushing sugar that is in cubes or large crystals increases the surface area. In general, the more finely divided a substance is, the greater the surface area per unit mass and the more quickly it dissolves. Figure 13-6 shows a model of solutions that are made from the same solute but have a different amount of surface area exposed to the solvent.

Agitating a Solution

Very close to the surface of a solute, the concentration of dissolved solute is high. Stirring or shaking helps to disperse the solute particles

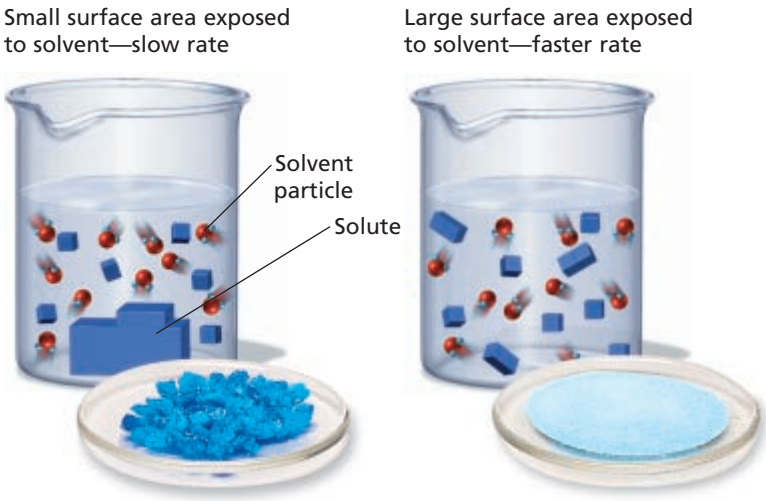
Small surface area exposed to solvent—slow rate
Large surface area exposed to solvent—faster rate
Solvent particle
Solute
$CuSO_4 \cdot 5H_2O$ large crystals
$CuSO_4 \cdot 5H_2O$ powdered
Increased surface area

FIGURE 13-6 The rate at which a solid solute dissolves can be increased by increasing the surface area. A powdered solute has a greater surface area exposed to solvent particles and therefore dissolves faster than a solute in large crystals.

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and bring fresh solvent into contact with the solute surface. Thus, the effect of stirring is similar to that of crushing a solid—contact between the solvent and the solute surface is increased.

Heating a Solvent

You have probably noticed that sugar and many other materials dissolve more quickly in warm water than in cold water. As the temperature of the solvent increases, solvent molecules move faster, and their average kinetic energy increases. Therefore, at higher temperatures, collisions between the solvent molecules and the solute are more frequent and are of higher energy than at lower temperatures. This helps to separate solute molecules from one another and to disperse them among the solvent molecules.

Solubility

If you add spoonful after spoonful of sugar to tea, eventually no more sugar will dissolve. For every combination of solvent with a solid solute at a given temperature, there is a limit to the amount of solute that can be dissolved. The point at which this limit is reached for any solute-solvent combination is difficult to predict precisely and depends on the nature of the solute, the nature of the solvent, and the temperature.

The following model describes why there is a limit. When solid sugar is first dropped into the water, sugar molecules leave the solid surface and move about at random in the solvent. Some of these dissolved molecules may collide with the crystal and remain there (recrystallize). As more of the solid dissolves and the concentration of dissolved molecules increases, these collisions become more frequent. Eventually, molecules are returning to the crystal at the same rate at which they are going into solution, and a dynamic equilibrium is established between dissolution and crystallization, as represented by the model in Figure 13-7.

Solution equilibrium *is the physical state in which the opposing processes of dissolution and crystallization of a solute occur at equal rates.*

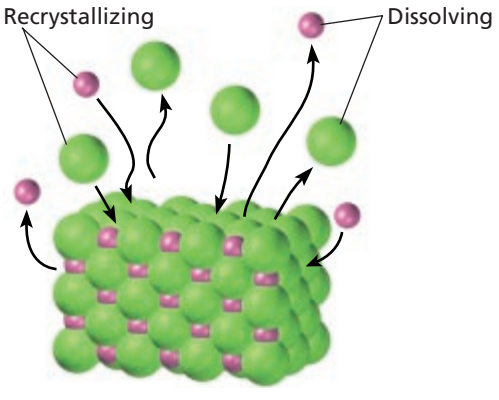

FIGURE 13-7 A saturated solution in a closed system is at equilibrium. The solute is recrystallizing at the same rate that it is dissolving, even though it appears that there is no activity in the system.

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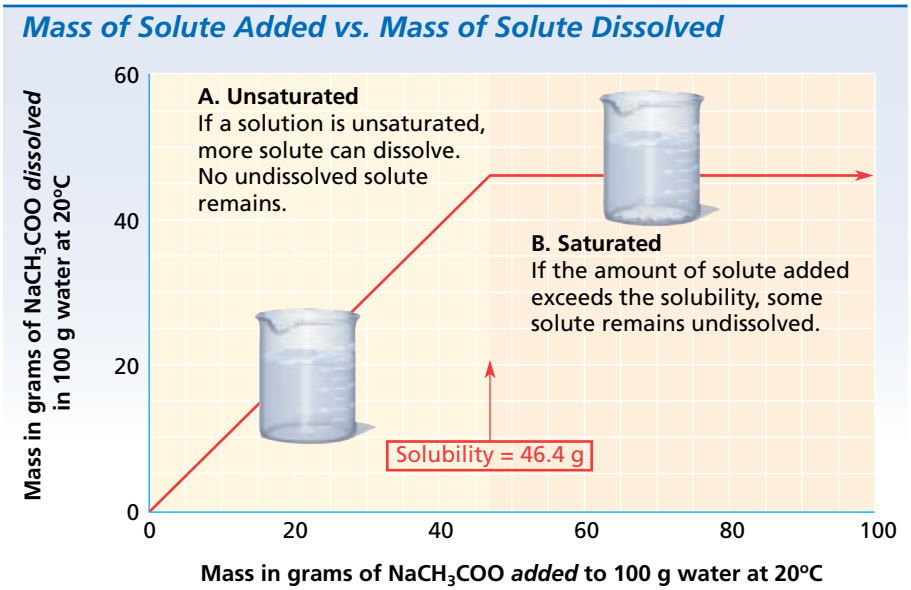
Mass of Solute Added vs. Mass of Solute Dissolved
Mass in grams of NaCH3COO dissolved in 100 g water at 20°C
60
40
20
0
A. Unsaturated
If a solution is unsaturated, more solute can dissolve. No undissolved solute remains.
B. Saturated
If the amount of solute added exceeds the solubility, some solute remains undissolved.
Solubility = 46.4 g
0
20
40
60
80
100
Mass in grams of NaCH3COO added to 100 g water at 20°C

FIGURE 13-8 The graph shows the range of solute masses that will produce an unsaturated solution. Once the saturation point is exceeded, the system will contain undissolved solute.

Saturated vs. Unsaturated Solutions

A solution that contains the maximum amount of dissolved solute is described as a **saturated solution.** How can you tell that the NaCl solution pictured in Figure 13-8 is saturated? If more sodium chloride is added to the solution, it falls to the bottom and does not dissolve because an equilibrium has been established between molecules leaving and entering the solid phase. If more water is added to the saturated solution, then more sodium chloride will dissolve in it. At 20°C, 35.9 g of NaCl is the maximum amount that will dissolve in 100. g of water. *A solution that contains less solute than a saturated solution under the existing conditions is an* **unsaturated solution.**

Supersaturated Solutions

When a saturated solution of a solute whose solubility increases with temperature is cooled, the excess solute usually comes out of solution, leaving the solution saturated at the lower temperature. But sometimes, if the solution is left to cool undisturbed, the excess solute does not separate and a supersaturated solution is produced. *A* **supersaturated solution** *is a solution that contains more dissolved solute than a saturated solution contains under the same conditions.* A supersaturated solution may remain unchanged for a long time if it is not disturbed, but once crystals begin to form, the process continues until equilibrium is reestablished at the lower temperature. An example of a supersaturated solution is one prepared from a saturated solution of sodium thiosulfate, $Na_2S_2O_3$, or sodium acetate, $NaCH_3COO$. Solute is added to hot water until the solution is saturated, and the hot solution is filtered. The filtrate is left to stand undisturbed as it cools. Dropping a small crystal of the solute into the supersaturated solution ("seeding") or disturbing the solution causes a rapid formation of crystals by the excess solute.

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Solubility Values

The **solubility** *of a substance is the amount of that substance required to form a saturated solution with a specific amount of solvent at a specified temperature*. The solubility of sugar, for example, is 204 g per 100. g of water at 20.°C. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubilities must be determined experimentally, and they vary widely, as illustrated in Table 13-4. Solubility values can be found in chemical handbooks and are usually given as grams of solute per 100. g of solvent or per 100. mL of solvent at a given temperature.

The rate at which a solid dissolves is unrelated to solubility. The maximum amount of solute that dissolves and reaches equilibrium is always the same under the same conditions.

Solute-Solvent Interactions

Lithium chloride is highly soluble in water, but gasoline is not. On the other hand, gasoline mixes readily with benzene, C_6H_6, but lithium chloride does not. Why are there such differences in solubility?

"Like dissolves like" is a rough but useful rule for predicting whether one substance will dissolve in another. What makes substances similar depends on the type of bonding, the polarity or nonpolarity of molecules, and the intermolecular forces between the solute and solvent.

TABLE 13-4 ***Solubility of Solutes as a Function of Temperature (in g solute/100. g H_2O)***

	Temperature (°C)					
Substance	**0**	**20**	**40**	**60**	**80**	**100**
$AgNO_3$	122	216	311	440	585	733
$Ba(OH)_2$	1.67	3.89	8.22	20.94	101.4	—
$C_{12}H_{22}O_{11}$	179	204	238	287	362	487
$Ca(OH)_2$	0.189	0.173	0.141	0.121	—	0.07
$Ce_2(SO_4)_3$	20.8	10.1	—	3.87	—	—
KCl	28.0	34.2	40.1	45.8	51.3	56.3
KI	128	144	162	176	192	206
KNO_3	13.9	31.6	61.3	106	167	245
LiCl	69.2	83.5	89.8	98.4	112	128
Li_2CO_3	1.54	1.33	1.17	1.01	0.85	0.72
NaCl	35.7	35.9	36.4	37.1	38.0	39.2
$NaNO_3$	73	87.6	102	122	148	180
CO_2 (gas at SP)	0.335	0.169	0.0973	0.058	—	—
O_2 (gas at SP)	0.00694	0.00537	0.00308	0.00227	0.00138	0.00

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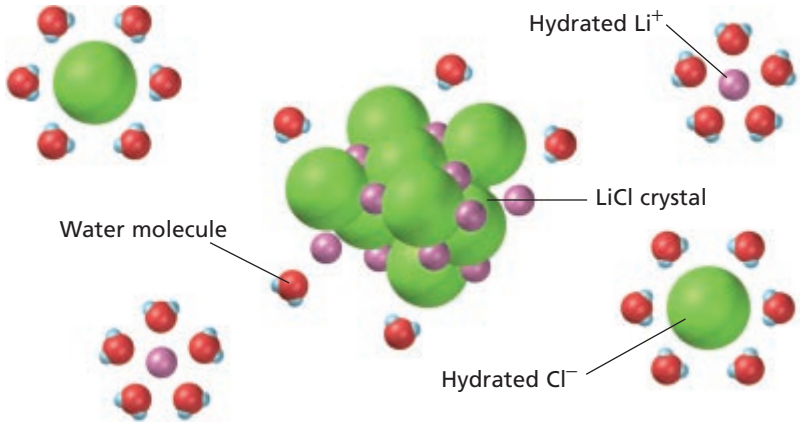

FIGURE 13-9 When LiCl dissolves, the ions are hydrated. The attraction between ions and water molecules is strong enough that each ion in solution is surrounded by water molecules.

Dissolving Ionic Compounds in Aqueous Solution

The polarity of water molecules plays an important role in the formation of solutions of ionic compounds in water. The charged ends of water molecules attract the ions in the ionic compounds and surround them to keep them separated from the other ions in the solution. Suppose we drop a few crystals of lithium chloride into a beaker of water. At the crystal surfaces, water molecules come into contact with Li^+ and Cl^- ions. The positive ends of the water molecules are attracted to Cl^- ions, while the negative ends are attracted to Li^+ ions. The attraction between water molecules and the ions is strong enough to draw the ions away from the crystal surface and into solution, as illustrated in Figure 13-9. *This solution process with water as the solvent is referred to as* **hydration.** The ions are said to be *hydrated.* As hydrated ions diffuse into the solution, other ions are exposed and are drawn away from the crystal surface by the solvent. The entire crystal gradually dissolves, and hydrated ions become uniformly distributed in the solution.

When crystallized from aqueous solutions, some ionic substances form crystals that incorporate water molecules. These crystalline compounds, known as *hydrates,* retain specific ratios of water molecules and are represented by formulas such as $CuSO_4 \cdot 5H_2O$. Heating the crystals of a hydrate can drive off the water of hydration and leave the anhydrous salt. When a crystalline hydrate dissolves in water, the water of hydration returns to the solvent. The behavior of a solute in its hydrated form is no different from the behavior of the anhydrous form. Dissolving either form results in a system containing hydrated ions and water.

Nonpolar Solvents

Ionic compounds are generally not soluble in nonpolar solvents such as carbon tetrachloride, CCl_4, and toluene, $C_6H_5CH_3$. The nonpolar solvent molecules do not attract the ions of the crystal strongly enough to overcome the forces holding the crystal together.

Would you expect lithium chloride to dissolve in toluene? No, LiCl is not soluble in toluene. LiCl and $C_6H_5CH_3$ differ widely in bonding, polarity, and intermolecular forces.

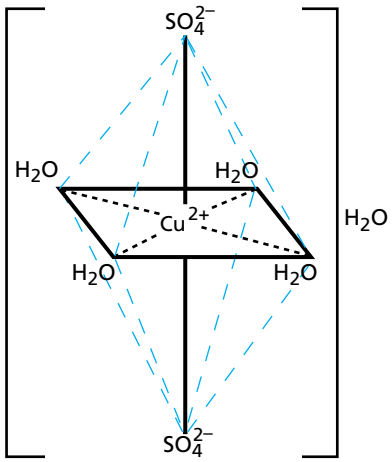

FIGURE 13-10 Hydrated copper(II) sulfate has water trapped in the crystal structure. Heating releases the water and produces the anhydrous form of the substance, which has the formula $CuSO_4$.

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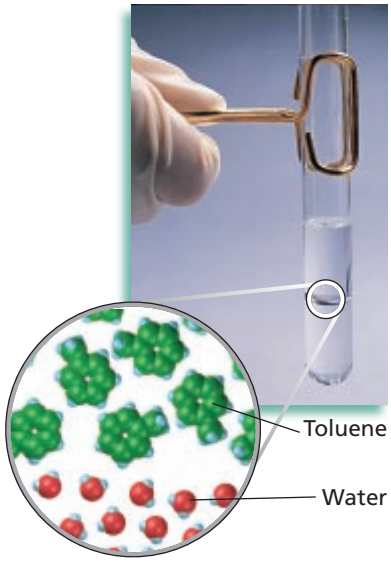


Insoluble and immiscible

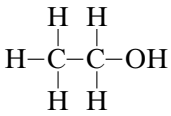
FIGURE 13-11 Toluene and water are immiscible. The components of this system exist in two distinct phases.

Liquid Solutes and Solvents

When you shake a bottle of salad dressing, oil droplets become dispersed in the water. As soon as you stop shaking the bottle, the strong attraction between the water molecules squeezes out the oil droplets, forming separate layers. *Liquid solutes and solvents that are not soluble in each other are* **immiscible.** Toluene and water, shown in Figure 13-11, are another example of immiscible substances.

Nonpolar substances, such as fats, oils, and greases, are generally quite soluble in nonpolar liquids, such as carbon tetrachloride, toluene, and gasoline. The only attractions between the nonpolar molecules are relatively weak London forces. The intermolecular forces existing in the solution are therefore very similar to those in pure substances. Thus, the molecules can mix freely with one another.

Liquids that dissolve freely in one another in any proportion are said to be completely **miscible.** Benzene and carbon tetrachloride are completely miscible. The nonpolar molecules of these substances exert no strong forces of attraction or repulsion, and the molecules mix freely. Ethanol and water, shown in Figure 13-12, also mix freely, but for a different reason. The −OH group on an ethanol molecule is somewhat polar. This group can form hydrogen bonds with water as well as with other ethanol molecules. The intermolecular forces in the mixture are so similar to those in the pure liquids that the liquids are mutually soluble in all proportions.

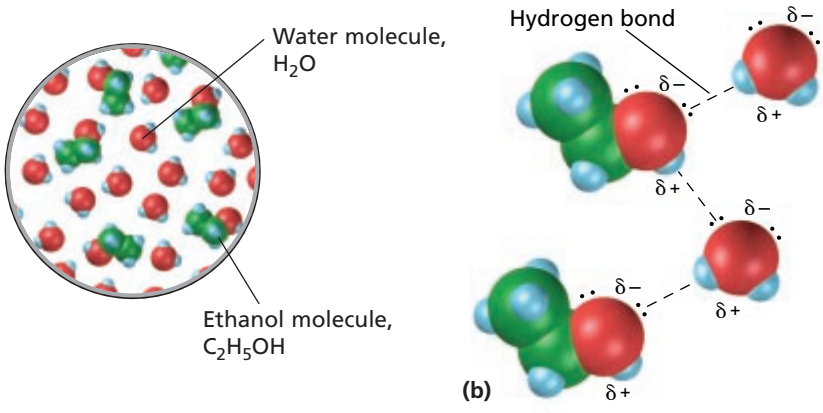


Gasoline contains mainly nonpolar hydrocarbons and is also an excellent solvent for fats, oils, and greases. The major intermolecular forces acting between the nonpolar molecules are relatively weak London forces.

Ethanol is intermediate in polarity between water and carbon tetrachloride. It is not as good a solvent for polar or ionic substances as water is. Sodium chloride is only slightly soluble in ethanol. On the other hand, ethanol is a better solvent than water is for less-polar substances because the molecule has a nonpolar region.

FIGURE 13-12 (a) Water and ethanol are miscible. The components of this system exist in a single phase with a uniform arrangement. (b) Hydrogen bonding between the solute and solvent enhances the solubility of ethanol in water.

(a) Soluble and miscible



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Effects of Pressure on Solubility

Changes in pressure have very little effect on the solubilities of liquids or solids in liquid solvents. However, increases in pressure increase gas solubilities in liquids.

When a gas is in contact with the surface of a liquid, gas molecules can enter the liquid. As the amount of dissolved gas increases, some molecules begin to escape and reenter the gas phase. An equilibrium is eventually established between the rates at which gas molecules enter and leave the liquid phase. As long as this equilibrium is undisturbed, the solubility of the gas in the liquid is unchanged at a given pressure.

$$\text{gas} + \text{solvent} \rightleftharpoons \text{solution}$$

Increasing the pressure of the solute gas above the solution puts stress on the equilibrium. Molecules collide with the liquid surface more often. The increase in pressure is partially offset by an increase in the rate of gas molecules entering the solution. In turn, the increase in the amount of dissolved gas causes an increase in the rate at which molecules escape from the liquid surface and become vapor. Eventually, equilibrium is restored at a higher gas solubility. As expected from Le Châtelier's principle, an increase in gas pressure causes the equilibrium to shift so that fewer molecules are in the gas phase.

Henry's Law

The solubility of a gas in a liquid is directly proportional to the partial pressure of that gas on the surface of the liquid. This is a statement of **Henry's law,** named after the English chemist William Henry. Henry's law applies to gas-liquid solutions at constant temperature.

Recall that when a mixture of ideal gases is confined in a constant volume at a constant temperature, each gas exerts the same pressure it would exert if it occupied the space alone. Assuming that the gases do not react in any way, each gas dissolves to the extent it would dissolve if no other gases were present.

In carbonated beverages, the solubility of CO_2 is increased by increasing the pressure. At the bottling plant, carbon dioxide gas is forced into the solution of flavored water at a pressure of 5–10 atm. The gas-in-liquid solution is then sealed in bottles or cans. When the cap is removed, the pressure is reduced to 1 atm, and some of the carbon dioxide escapes as gas bubbles. *The rapid escape of a gas from a liquid in which it is dissolved is known as* **effervescence** and is shown in Figure 13-13.

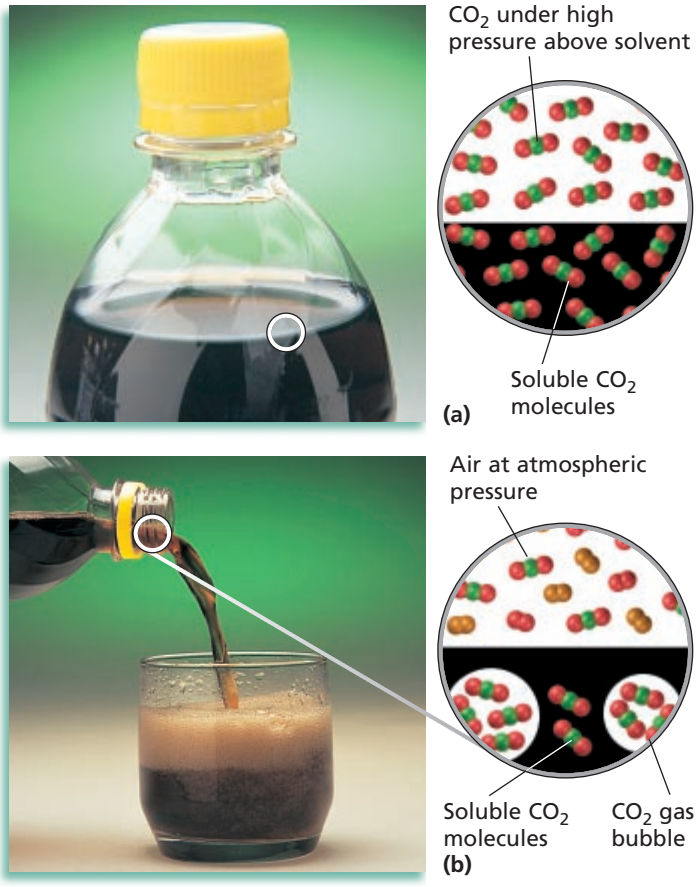

FIGURE 13-13 (a) There are no gas bubbles in the unopened bottle of soda because the pressure of CO_2 applied during bottling keeps the carbon dioxide gas dissolved in the liquid. (b) When the cap on the bottle is removed, the pressure of CO_2 on the liquid is reduced, and CO_2 can escape from the liquid. The soda effervesces when the bottle is opened and the pressure is reduced.

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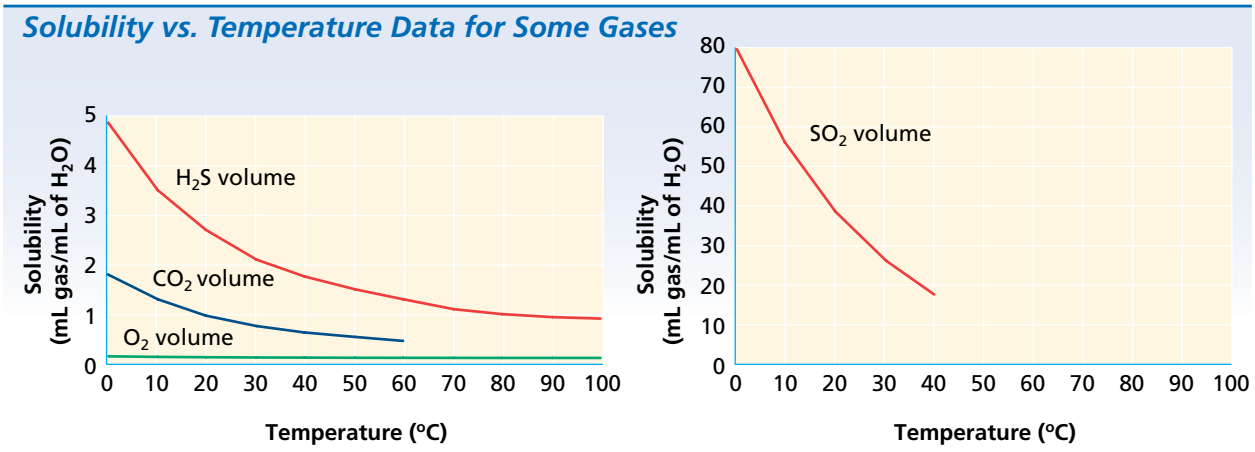

FIGURE 13-14 The solubility of gases in water decreases with increasing temperature. Which gas has the greater solubility at 30°C—CO_2 or SO_2?

Effects of Temperature on Solubility

First let's consider gas solubility. Increasing the temperature usually decreases gas solubility. As the temperature increases, the average kinetic energy of the molecules in solution increases. A greater number of solute molecules are able to escape from the attraction of solvent molecules and return to the gas phase. At higher temperatures, therefore, equilibrium is reached with fewer gas molecules in solution and gases are generally less soluble, as shown in Figure 13-14.

The effect of temperature on the solubility of solids in liquids is more difficult to predict. Often, increasing the temperature increases the solubility of solids. However, an equivalent temperature increase can

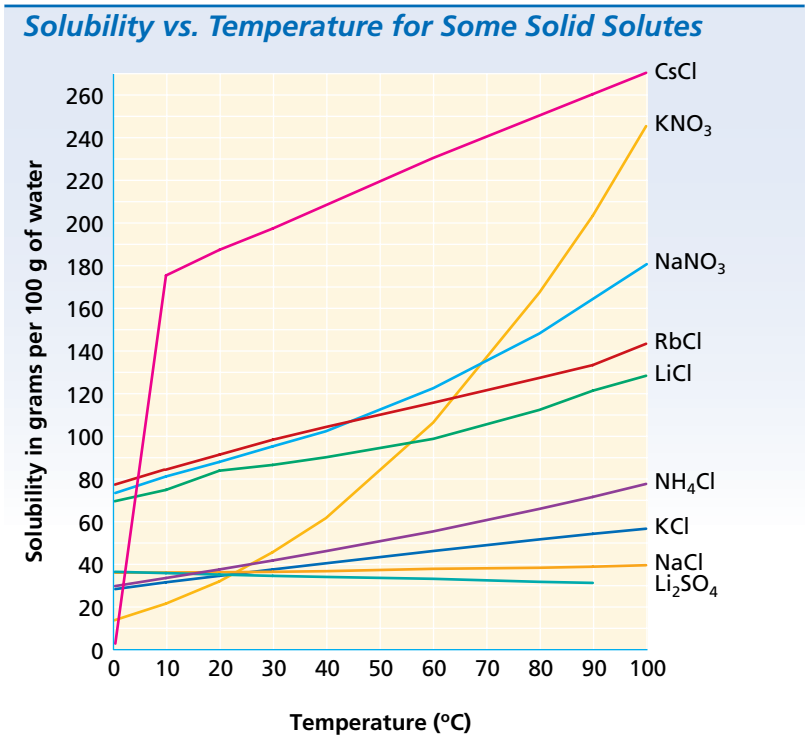

FIGURE 13-15 Solubility curves for various solid solutes generally show increasing solubility with increases in temperature. From the graph, you can see that the solubility of $NaNO_3$ is affected more by temperature than is NaCl.

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result in a large increase in solubility in one case and only a slight increase in another.

In Table 13-4 and Figure 13-15, compare the effect of temperature on the solubilities of potassium nitrate, KNO_3, and sodium chloride, NaCl. About 14 g of potassium nitrate will dissolve in 100. g of water at 0.°C. The solubility of potassium nitrate increases by more than 150 g KNO_3 per 100. g H_2O when the temperature is raised to 80.°C. Under similar circumstances, the solubility of sodium chloride increases by only about 2 g NaCl per 100. g H_2O. In some cases, solubility of a solid *decreases* with an increase in temperature. For example, between 0.°C and 60.°C the solubility of cerium sulfate, $Ce_2(SO_4)_3$, decreases by about 17 g.

Heats of Solution

The formation of a solution is accompanied by an energy change. If you dissolve some potassium iodide, KI, in water, you will find that the outside of the container feels cold to the touch. But if you dissolve some lithium chloride, LiCl, in the same way, the outside of the container feels hot. The formation of a solid-liquid solution can apparently either absorb heat (KI in water) or release heat (LiCl in water).

During the formation of a solution, solvent and solute particles experience changes in the forces attracting them to other particles. Before dissolving begins, solvent molecules are held together by intermolecular forces (solvent-solvent attraction). In the solute, molecules are held together by intermolecular forces (solute-solute attraction). Energy is required to separate solute molecules and solvent molecules from their neighbors. *A solute particle that is surrounded by solvent molecules,* as shown by the model in Figure 13-9, *is said to be* **solvated.**

Solution formation can be pictured as the result of the three interactions summarized in Figure 13-16.

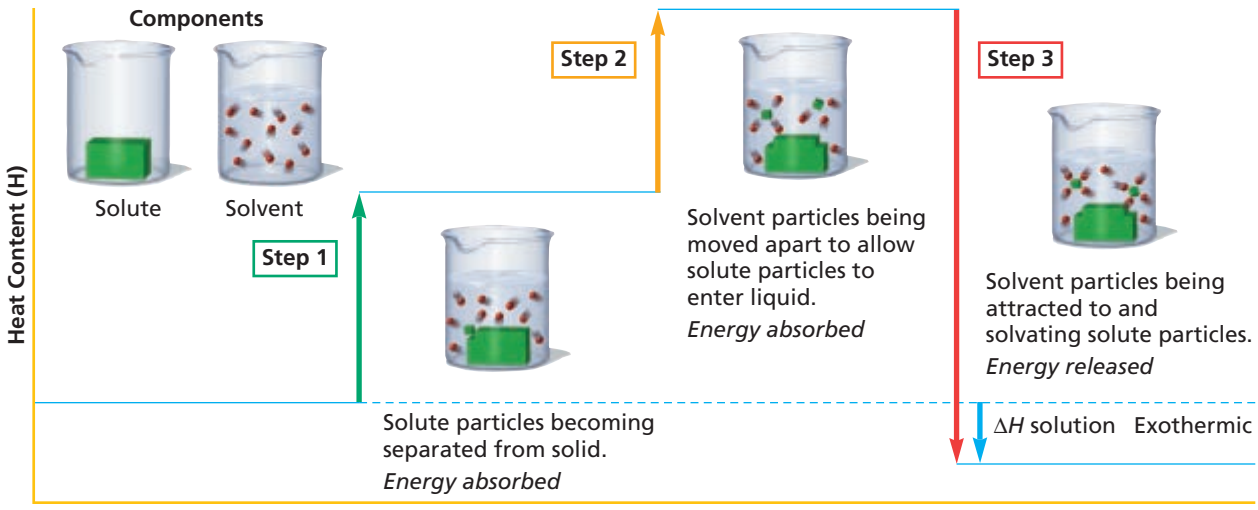

FIGURE 13-16 The graph shows the changes in the heat content that occur during the formation of a solution. How would the graph differ for a system with an endothermic heat of solution?

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TABLE 13-5 Heats of Solution (kJ/mol solute at 25°C)

Substance	Heat of solution	Substance	Heat of solution
$AgNO_3(s)$	+22.59	$KOH(s)$	–57.61
$CH_3COOH(l)$	–1.51	$LiCl(s)$	–37.03
$HCl(g)$	–74.84	$MgSO_4(s)$	+15.9
$HI(g)$	–81.67	$NaCl(s)$	+3.88
$KCl(s)$	+17.22	$NaNO_3(s)$	+20.50
$KClO_3(s)$	+41.38	$NaOH(s)$	–44.51
$KI(s)$	+20.33	$NH_3(g)$	–30.50
$KNO_3(s)$	+34.89	$NH_4Cl(s)$	+14.78
		$NH_4NO_3(s)$	+25.69

The net amount of heat energy absorbed or released when a specific amount of solute dissolves in a solvent is the **heat of solution.** From the model in Figure 13-16, you can see that the heat of solution is negative (heat is released) when the sum of attractions from Steps 1 and 2 is less than Step 3. The heat of solution is positive (heat is absorbed) when the sum of attractions from Steps 1 and 2 is greater than Step 3.

You know that heating decreases the solubility of a gas, so dissolution of gases is exothermic. How do the values for the heats of solution in Table 13-5 support this idea of exothermic solution processes for gaseous solutes?

In the gaseous state, molecules are so far apart that there are virtually no intermolecular forces of attraction between them. Therefore, the solute-solute interaction has little effect on the heat of a solution of a gas. Energy is released when a gas dissolves in a liquid because attraction between solute gas and solvent molecules outweighs the energy needed to separate solvent molecules.

SECTION REVIEW

1. Why would you expect a packet of sugar to dissolve faster in hot tea than in iced tea?
2. a. Explain how you would prepare a saturated solution of sugar in water. b. How would you then make it a supersaturated solution?
3. Explain why ethanol will dissolve in water and carbon tetrachloride will not.
4. When a solute molecule is solvated, is heat released or absorbed?
5. If a warm bottle of soda and a cold bottle of soda are opened, which will effervesce more and why?

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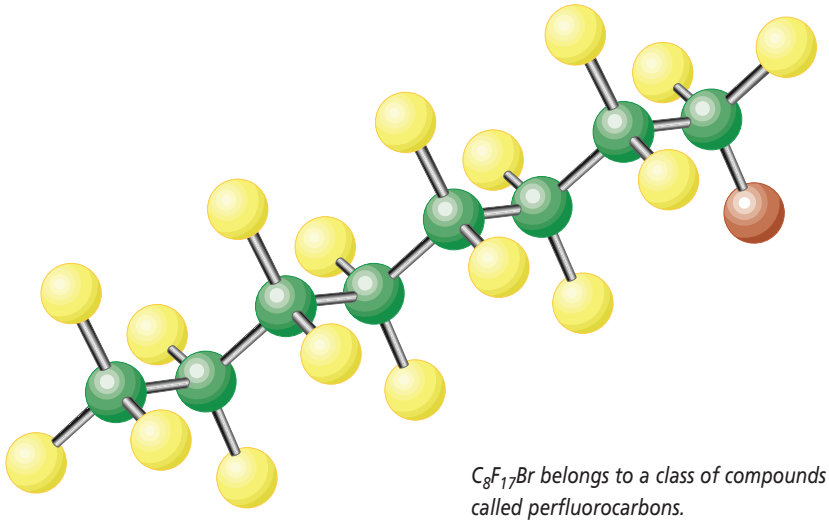
Artificial Blood

A patient lies bleeding on a stretcher. The doctor leans over to check the patient's wounds and barks an order to a nearby nurse: "Get him a unit of artificial blood, stat!" According to Dr. Peter Keipert, Program Director of Oxygen Carriers Development at Alliance Pharmaceutical Corp., this scenario may soon be commonplace thanks to a synthetic solution that can perform one of the main functions of human blood—transporting oxygen.

The hemoglobin inside red blood cells collects oxygen in our lungs, transports the oxygen to all the tissues of the body, and then takes carbon dioxide back to the lungs. Dr. Keipert's blood substitute accomplishes the same task, but it uses oily chemicals called perfluorocarbons instead of hemoglobin to transport the oxygen. The perfluorocarbons are carried in a water-based saline solution, but because oil and water do not mix, a bonding chemical called a surfactant is added to hold the mixture together. The perfluorocarbons are sheared into tiny droplets and then coated with the bonding molecules. One end of these molecules attaches to the perfluorocarbon, and the other end attaches to the water, creating a milky solution. The blood-substitute solution, called Oxygent™, is administered to a patient in the same way regular blood is. The perfluorocarbons are eventually exhaled through the lungs.



$C_8F_{17}Br$ belongs to a class of compounds called perfluorocarbons.

Dr. Keipert is quick to point out that Oxygent is not a true artificial blood. The solution only functions to carry gases to and from tissues; it cannot clot or perform any of the immune-system functions that blood does. Still, the substitute has several advantages over real blood. Oxygent has a shelf life of more than a year. Oxygent also eliminates many of the risks associated with blood transfusions. Because the substitute can dissolve larger amounts of oxygen than real blood can, smaller amounts of the solution are needed.

Oxygent is currently being tested in surgical patients.

"Once this product is approved and has been demonstrated to be safe and effective in elective surgery, I think you will see its use spread into the emergency critical-care arena," says Dr. Keipert. "A patient who has lost a lot of blood and who is currently being resuscitated with normal fluids like saline solutions would be given Oxygent as an additional oxygen-delivery agent in the emergency room."

How will the approval of Oxygent benefit the medical community?

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SECTION 13-3

Objectives

- Given the mass of solute and volume of solvent, calculate the concentration of a solution.
- Given the concentration of a solution, determine the amount of solute in a given amount of solution.
- Given the concentration of a solution, determine the amount of solution that contains a given amount of solute.

Concentration of Solutions

The **concentration** *of a solution is a measure of the amount of solute in a given amount of solvent or solution.* Some medications are solutions of drugs—a one-teaspoon dose at the correct concentration might cure the patient, while the same dose in the wrong concentration might kill the patient.

In this section, we introduce two different ways of expressing the concentrations of solutions: molarity and molality.

Sometimes solutions are referred to as "dilute" or "concentrated," but these are not very definite terms. "Dilute" just means that there is a relatively small amount of solute in a solvent. "Concentrated," on the other hand, means that there is a relatively large amount of solute in a solvent. Note that these terms are unrelated to the degree to which a solution is saturated. A saturated solution of a substance that is not very soluble might be very dilute.

Molarity

Molarity *is the number of moles of solute in one liter of solution.* To find the molarity of a solution, you must know the molar mass of the solute. For example, a "one-molar" solution of sodium hydroxide, NaOH, contains one mole of NaOH in every liter of solution. The symbol for molarity is M, and the concentration of a one-molar solution of sodium hydroxide is written as 1 M NaOH.

One mole of NaOH has a mass of 40.0 g. If this quantity of NaOH is dissolved in enough water to make exactly 1.00 L of solution, the solution is a 1 M solution. If 20.0 g of NaOH, which is 0.500 mol, is dissolved in enough water to make 1.00 L of solution, a 0.500 M NaOH solution is produced. This relationship between molarity, moles, and volume may be expressed in the following ways.

$$\text{molarity (M)} = \frac{\text{amount of solute (mol)}}{\text{volume of solution (L)}}$$

$$= \frac{0.500 \text{ mol NaOH}}{1.00 \text{ L}}$$

$$= 0.500 \text{ M NaOH}$$

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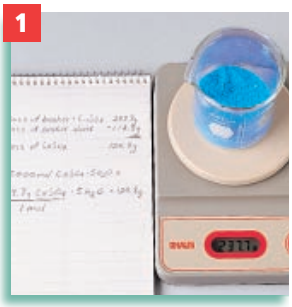
If twice the molar mass of NaOH, 80.0 g, is dissolved in enough water to make 1 L of solution, a 2 M solution is produced. The molarity of any solution can be calculated by dividing the number of moles of solute by the number of liters of solution.

Note that a 1 M solution is *not* made by adding 1 mol of solute to 1 L of *solvent*. In such a case, the final total volume of the solution would not be 1 L. Instead, 1 mol of solute is first dissolved in less than 1 L of solvent. Then the resulting solution is carefully diluted with more solvent to bring the *total volume* to 1 L, as shown in Figure 13-17. The following sample problem will show you how molarity is often used.

FIGURE 13-17 The preparation of a 0.5000 M solution of $CuSO_4 \cdot 5H_2O$ starts with calculating the mass of solute needed.



Start by calculating the mass of $CuSO_4 \cdot 5H_2O$ needed. Making a liter of this solution requires 0.5000 mol of solute. Convert the moles to mass by multiplying by the molar mass of $CuSO_4 \cdot 5H_2O$. This mass is calculated to be 124.8 g.

Add some solvent to the solute to dissolve it, then pour it into a 1.0 L volumetric flask.

Rinse the weighing beaker with more solvent to remove all the solute, and pour the rinse into the flask. Add water until the volume of the solution nears the neck of the flask.

Put the stopper in the flask, and swirl the solution thoroughly.

Carefully fill the flask to the 1.0 L mark with water.

Restopper the flask and invert it at least 10 times to ensure complete mixing.

The resulting solution has 0.5000 mol of solute dissolved in 1.000 L of solution, which is a 0.5000 M concentration.

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SAMPLE PROBLEM 13-1

You have 3.50 L of solution that contains 90.0 g of sodium chloride, NaCl. What is the molarity of that solution?

SOLUTION

1 ANALYZE

Given: solute mass = 90.0 g NaCl
solution volume = 3.50 L

Unknown: molarity of NaCl solution

2 PLAN

Molarity is the number of moles of solute per liter of solution. The solute is described in the problem by mass, not the amount in moles. You need one conversion (grams to moles of solute) using the inverted molar mass of NaCl to arrive at your answer.

$$\text{grams of solute} \longrightarrow \text{number of moles of solute} \longrightarrow \text{molarity}$$

$$\text{g NaCl} \times \frac{1 \text{ mol NaCl}}{\text{g NaCl}} = \text{mol NaCl}$$

$$\frac{\text{amount of solute (mol)}}{V \text{ solution (L)}} = \text{molarity of solution (M)}$$

3 COMPUTE

You will need the molar mass of NaCl.
NaCl = 58.44 g/mol

$$90.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 1.54 \text{ mol NaCl}$$

$$\frac{1.54 \text{ mol NaCl}}{3.50 \text{ L of solution}} = 0.440 \text{ M NaCl}$$

4 EVALUATE

Because each factor involved is limited to three significant digits, the answer should have three significant digits, which it does. The units cancel correctly to give the desired moles of solute per liter of solution, which is molarity.

SAMPLE PROBLEM 13-2

You have 0.8 L of a 0.5 M HCl solution. How many moles of HCl does this solution contain?

SOLUTION

1 ANALYZE

Given: volume of solution = 0.8 L
concentration of solution = 0.5 M HCl

Unknown: moles of HCl in a given volume

2 PLAN

The molarity indicates the moles of solute that are in one liter of solution. Given the volume of the solution, the number of moles of solute can then be found.

$$\text{concentration (mol of HCl/L of solution)} \times \text{volume (L of solution)} = \text{mol of HCl}$$

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3 COMPUTE

$$\frac{0.5 \text{ mol HCl}}{1.0 \text{ L of solution}} \times 0.8 \text{ L of solution} = 0.4 \text{ mol HCl}$$

4 EVALUATE

The answer is correctly given to one significant digit. The units cancel correctly to give the desired unit, mol. There should be less than 0.5 mol HCl, because less than 1 L of solution was used.

SAMPLE PROBLEM 13-3

To produce 40.0 g of silver chromate, you will need at least 23.4 g of potassium chromate in solution as a reactant. All you have on hand in the stock room is 5 L of a 6.0 M K_2CrO_4 solution. What volume of the solution is needed to give you the 23.4 g K_2CrO_4 needed for the reaction?

SOLUTION

1 ANALYZE

Given: volume of solution = 5 L
concentration of solution = 6.0 M K_2CrO_4
mass of solute = 23.4 g K_2CrO_4
mass of product = 40.0 g Ag_2CrO_4

Unknown: volume of K_2CrO_4 solution in L

2 PLAN

The molarity indicates the moles of solute that are in 1 L of solution. Given the mass of solute needed, the amount in moles of solute can then be found. Use the molarity and the amount in moles of K_2CrO_4 to determine the volume of K_2CrO_4 that will provide 23.4 g.

grams of solute $\longrightarrow$ moles solute
moles solute and molarity $\longrightarrow$ liters of solution needed

3 COMPUTE

To get the moles of solute, you'll need to calculate the molar mass of K_2CrO_4.

$$1 \text{ mol } K_2CrO_4 = 194.2 \text{ g } K_2CrO_4$$

$$23.4 \text{ g } K_2CrO_4 = \frac{1.0 \text{ mol } K_2CrO_4}{194.2 \text{ g } K_2CrO_4} = 0.120 \text{ mol } K_2CrO_4$$

$$6.0 \text{ M } K_2CrO_4 = \frac{0.120 \text{ mol } K_2CrO_4}{x \text{ L } K_2CrO_4 \text{ soln}}$$

$$x = 0.020 \text{ L } K_2CrO_4 \text{ soln}$$

4 EVALUATE

The answer is correctly given to two significant digits. The units cancel correctly to give the desired unit, liters of solution.

PRACTICE

1. What is the molarity of a solution composed of 5.85 g of potassium iodide, KI, dissolved in enough water to make 0.125 L of solution? *Answer* 0.282 M KI
2. How many moles of H_2SO_4 are present in 0.500 L of a 0.150 M H_2SO_4 solution? *Answer* 0.0750 mol
3. What volume of 3.00 M NaCl is needed for a reaction that requires 146.3 g of NaCl? *Answer* 0.834 L

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Molality

Molality *is the concentration of a solution expressed in moles of solute per kilogram of solvent.* A solution that contains 1 mol of solute, sodium hydroxide, NaOH, for example, dissolved in exactly 1 kg of solvent is a "one-molal" solution. The symbol for molality is *m,* and the concentration of this solution is written as 1 *m* NaOH.

One mole of NaOH has a molar mass of 40.0 g, so 40.0 g of NaOH dissolved in 1 kg of water results in a one-molal NaOH solution. If 20.0 g of NaOH, which is 0.500 mol of NaOH, is dissolved in exactly 1 kg of water, the concentration of the solution is 0.500 *m* NaOH.

$$\text{molality} = \frac{\text{moles solute}}{\text{mass of solvent (kg)}}$$

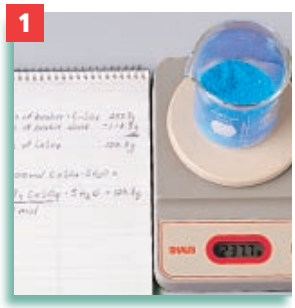
$$\frac{0.500 \text{ mol NaOH}}{1 \text{ kg } H_2O} = 0.500 \ m \text{ NaOH}$$

If 80.0 g of sodium hydroxide, which is 2 mol, is dissolved in 1 kg of water, a 2.00 *m* solution of NaOH is produced. The molality of any solution can be found by dividing the number of moles of solute by the mass in kilograms of the solvent in which it is dissolved. Note that if the amount of solvent is expressed in grams, the mass of solvent must be converted to kilograms by multiplying by the following conversion factor.

$$1 \text{ kg}/1000 \text{ g}$$

Figure 13-18 shows how a 0.5000 *m* solution of $CuSO_4 \cdot 5H_2O$ is prepared, in contrast with the 0.5000 M solution in Figure 13-17.

FIGURE 13-18 The preparation of a 0.5000 *m* solution of $CuSO_4 \cdot 5H_2O$ also starts with the calculation of the mass of solute needed.



Calculate the mass of $CuSO_4 \cdot 5H_2O$ needed. To make this solution, each kilogram of solvent (1000 g) will require 0.5000 mol of $CuSO_4 \cdot 5H_2O$. This mass is calculated to be 124.8 g.

Add exactly 1 kg of solvent to the solute in the beaker. Because the solvent is water, 1 kg will equal 1000 mL.

Mix thoroughly.

The resulting solution has 0.5000 mol of solute dissolved in 1 kg of solvent.

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Concentrations are expressed as molalities when studying properties of solutions related to vapor pressure and temperature changes. Molality is used because it does not change with changes in temperature. Below is a comparison of the equations for molarity and molality.

$$\text{molarity, M} = \frac{\text{amount of A (mol)}}{\text{volume of solution (L)}}$$

$$\text{molality, } m = \frac{\text{amount of A (mol)}}{\text{mass of solvent (kg)}}$$

SAMPLE PROBLEM 13-4

A solution was prepared by dissolving 17.1 g of sucrose (table sugar, $C_{12}H_{22}O_{11}$) in 125 g of water. Find the molal concentration of this solution.

SOLUTION

1 ANALYZE

Given: solute mass = 17.1 g $C_{12}H_{22}O_{11}$
solvent mass = 125 g H_2O

Unknown: molal concentration

2 PLAN

To find molality, you need moles of solute and kilograms of solvent. The given grams of sucrose must be converted to moles. The mass in grams of solvent must be converted to kilograms.

$$\text{mol } C_{12}H_{22}O_{11} = \frac{\text{g } C_{12}H_{22}O_{11}}{\text{molar mass } C_{12}H_{22}O_{11}}$$

$$\text{kg } H_2O = \text{g } H_2O \times \frac{1\text{ kg}}{1000\text{ g}}$$

$$\text{molality } C_{12}H_{22}O_{11} = \frac{\text{mol } C_{12}H_{22}O_{11}}{\text{kg } H_2O}$$

3 COMPUTE

Use the periodic table to compute the molar mass of $C_{12}H_{22}O_{11}$.
$C_{12}H_{22}O_{11} = 342.34$ g/mol

$$17.1\ \cancel{\text{g } C_{12}H_{22}O_{11}} \times \frac{1\text{ mol } C_{12}H_{22}O_{11}}{342.34\ \cancel{\text{g } C_{12}H_{22}O_{11}}} = 0.0500\text{ mol } C_{12}H_{22}O_{11}$$

$$\frac{125\ \cancel{\text{g}}\ H_2O}{1000\ \cancel{\text{g}}/\text{kg}} = 0.125\text{ kg } H_2O$$

$$\frac{0.0500\text{ mol } C_{12}H_{22}O_{11}}{0.125\text{ kg } H_2O} = 0.400\ m\ C_{12}H_{22}O_{11}$$

4 EVALUATE

The answer is correctly given to three significant digits. The unit mol solute/kg solvent is correct for molality.

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SAMPLE PROBLEM 13-5

A solution of iodine, I_2, in carbon tetrachloride, CCl_4, is used when iodine is needed for certain chemical tests. How much iodine must be added to prepare a 0.480 *m* solution of iodine in CCl_4 if 100.0 g of CCl_4 is used?

SOLUTION

1 ANALYZE

Given: molality of solution = 0.480 *m* I_2
mass of solvent = 100.0 g CCl_4
Unknown: mass of solute

2 PLAN

Your first step should be to convert the grams of solvent to kilograms. The molality gives you the moles of solute, which can be converted to the grams of solute using the molar mass of I_2.

3 COMPUTE

Use the periodic table to compute the molar mass of I_2.
$I_2 = 253.8$ g/mol

$$100.0 \text{ g } \cancel{CCl_4} \times \frac{1 \text{ kg}}{1000 \text{ g } \cancel{CCl_4}} = 0.100 \text{ kg } CCl_4$$

$$0.480 \ m = \frac{x \text{ mol } I_2}{0.1 \text{ kg } H_2O} \qquad x = 0.0480 \text{ mol } I_2$$

$$0.0480 \text{ } \cancel{\text{mol } I_2} \times \frac{253.8 \text{ g } I_2}{\cancel{\text{mol } I_2}} = 12.2 \text{ g } I_2$$

4 EVALUATE

The answer has three significant digits and the units for mass of I_2.

PRACTICE

1. What is the molality of a solution composed of 255 g of acetone, $(CH_3)_2CO$, dissolved in 200. g of water? *Answer* 22 *m* acetone
2. What quantity, in grams, of methanol, CH_3OH, is required to prepare a 0.244 *m* solution in 400. g of water? *Answer* 3.12 g CH_3OH
3. How many grams of $AgNO_3$ are needed to prepare a 0.125 *m* solution in 250. mL of water? *Answer* 5.31 g $AgNO_3$
4. What is the molality of a solution containing 18.2 g HCl and 250. g of water? *Answer* 2.00 *m*

SECTION REVIEW

1. What quantity represents the ratio of the number of moles of solute for a given volume of solution?
2. Five grams of sugar, $C_{12}H_{22}O_{11}$, are dissolved in water to make 1 L of solution. What is the concentration of this solution expressed as a molarity?

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CHAPTER 13 REVIEW

CHAPTER SUMMARY

13-1

- Solutions are homogeneous mixtures.
- Mixtures are classified as solutions, suspensions, or colloids, depending on the size of the solute particles in the mixture.
- The dissolved substance is the solute. Solutions that have water as a solvent are aqueous solutions.
- Solutions can consist of solutes and solvents that are solids, liquids, or gases.
- Suspensions settle out upon standing. Colloids do not settle out, and they scatter light that is shined through them.
- Most ionic solutes and some molecular solutes form aqueous solutions that conduct an electric current. These solutes are called electrolytes.
- Nonelectrolytes are solutes that dissolve in water to form solutions that do not conduct.

Vocabulary

colloid (397)
electrolyte (399)
nonelectrolyte (400)
soluble (395)
solute (396)
solution (396)
solvent (396)
suspension (397)

13-2

- A solute dissolves at a rate that depends on the surface area of the solute, how vigorously the solution is mixed, and the temperature of the solvent.
- The solubility of a substance indicates how much of that substance will dissolve in a specified amount of solvent under certain conditions.
- The solubility of a substance depends on the temperature.
- The solubility of gases in liquids increases with increases in pressure.
- The solubility of gases in liquids decreases with increases in temperature.
- The overall energy change per mole during solution formation is called the heat of solution.

Vocabulary

effervescence (407)
heat of solution (410)
Henry's law (407)
hydration (405)
immiscible (406)
miscible (406)
saturated solution (403)
solubility (404)
solvated (409)
solution equilibrium (402)
supersaturated solution (403)
unsaturated solution (403)

13-3

- Two useful expressions of concentration are molarity and molality.
- The molar concentration of a solution represents the ratio of moles of solute to liters of solution.
- The molal concentration of a solution represents the ratio of moles of solute to kilograms of solvent.

Vocabulary

concentration (412)
molality (416)
molarity (412)

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REVIEWING CONCEPTS

1. a. What is the Tyndall effect?
b. Identify one example of this effect. (13-1)

2. Given an unknown mixture consisting of two or more substances, explain one technique that could be used to determine whether that mixture is a true solution, a colloid, or a suspension. (13-1)

3. a. What is solution equilibrium?
b. What factors determine the point at which a given solute-solvent combination reaches equilibrium? (13-2)

4. a. What is a saturated solution?
b. What visible evidence indicates that a solution is saturated?
c. What is an unsaturated solution? (13-2)

5. a. What is meant by the solubility of a substance?
b. What condition(s) must be specified when expressing the solubility of a substance? (13-2)

6. a. What rule of thumb is useful for predicting whether one substance will dissolve in another?
b. Describe what the rule means in terms of various combinations of polar and nonpolar solutes and solvents. (13-2)

7. a. How does pressure affect the solubility of a gas in a liquid?
b. What law is a statement of this relationship? (13-1)
c. If the pressure of a gas above a liquid is increased, what happens to the amount of the gas that will dissolve in the liquid, if all other conditions remain constant?
d. Two bottles of soda are opened. One is a cold bottle and the other is partially frozen. Which system will show more effervescence and why? (13-2)

8. Based on Figure 13-15, determine the solubility of each of the following in grams of solute per 100. g H_2O.
a. $NaNO_3$ at 10°C
b. KNO_3 at 60°C
c. NaCl at 50°C (13-2)

9. Based on Figure 13-15, at what temperature would each of the following solubility levels be observed?
a. 40 g KCl in 100 g H_2O
b. 100 g $NaNO_3$ in 100 g H_2O
c. 50 g KNO_3 in 100 g H_2O (13-2)

10. The heat of solution for $AgNO_3$ is +22.8 kJ/mol.
a. Write the equation that represents the dissolution of $AgNO_3$ in water.
b. Is the dissolution process endothermic or exothermic? Is the crystallization process endothermic or exothermic?
c. As $AgNO_3$ dissolves, what change occurs in the temperature of the solution?
d. When the system is at equilibrium, how do the rates of dissolution and crystallization compare?
e. If the solution is then heated, how will the rates of dissolution and crystallization be affected? Why?
f. How will the increased temperature affect the amount of solute that can be dissolved?
g. If the solution is allowed to reach equilibrium and is then cooled, how will the system be affected? (13-2)

11. Under what circumstances might we prefer to express solution concentrations in terms of
a. molarity?
b. molality? (13-3)

12. What opposing forces are at equilibrium in the sodium chloride system shown in Figure 13-7? (13-2)

PROBLEMS

Solubility

13. Plot a solubility graph for $AgNO_3$ from the following data, with grams of solute (by increments of 50) per 100 grams of H_2O on the vertical axis and with temperature in °C on the horizontal axis.

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Grams solute per 100 g H_2O	Temperature (°C)
122	0
216	30
311	40
440	60
585	80
733	100

a. How does the solubility of $AgNO_3$ vary with the temperature of the water?
b. Estimate the solubility of $AgNO_3$ at 35°C, 55°C, and 75°C.
c. At what temperature would the solubility of $AgNO_3$ be 275 g per 100 g of H_2O?
d. If 100 g of $AgNO_3$ were added to 100 g of H_2O at 10°C, would the resulting solution be saturated or unsaturated? What would occur if 325 g of $AgNO_3$ were added to 100 g of H_2O at 35°C?

14. If a saturated solution of KNO_3 in 100. g of H_2O at 60°C is cooled to 20°C, approximately how many grams of the solute will precipitate out of the solution? (Use Table 13-4.)

Molarity

15. a. Suppose you wanted to dissolve 40.0 g NaOH in enough H_2O to make 6.00 L of solution.
(1) What is step 1 in solving the problem?
(2) What is the molar mass of NaOH?
(3) What is the molarity of this solution?
b. What is the molarity of a solution of 14.0 g NH_4Br in enough H_2O to make 150 mL of solution?

16. a. Suppose you wanted to produce 1.00 L of a 3.50 M solution of H_2SO_4.
(1) What is the solute?
(2) What is the solvent?
(3) How many grams of solute are needed to make this solution?
b. How many grams of solute are needed to make 2.50 L of a 1.75 M solution of $Ba(NO_3)_2$?

17. How many moles of NaOH are contained in 65.0 mL of a 2.20 M solution of NaOH in H_2O? (Hint: See Sample Problem 13-2.)

18. A solution is made by dissolving 26.42 g of $(NH_4)_2SO_4$ in enough H_2O to make 50.00 mL of solution.
a. What is the molar mass of $(NH_4)_2SO_4$?
b. What are the products of the solution?
c. What is the molarity of this solution?

19. Suppose you wanted to find out how many milliliters of 1.0 M $AgNO_3$ are needed to provide 169.88 g of pure $AgNO_3$.
a. What is step 1 in solving the problem?
b. What is the molar mass of $AgNO_3$?
c. How many milliliters of solution are needed?

20. a. Balance the equation:
$H_3PO_4 + Ca(OH)_2 \longrightarrow Ca_3(PO_4)_2 + H_2O$
b. What mass of each product results if 750 mL of 6.00 M H_3PO_4 reacts according to the equation?

21. How many milliliters of 18.0 M H_2SO_4 are required to react with 250. mL of 2.50 M $Al(OH)_3$ if the products are aluminum sulfate and water?

22. 75.0 mL of an $AgNO_3$ solution reacts with enough Cu to produce 0.250 g of Ag by single replacement. What is the molarity of the initial $AgNO_3$ solution if $Cu(NO_3)_2$ is the other product?

Molality

23. a. Suppose you wanted to dissolve 294.3 g H_2SO_4 in 1.000 kg H_2O.
(1) What is the solute?
(2) What is the solvent?
(3) What is the molality of this solution?
b. What is the molality of a solution of 63.0 g HNO_3 in 0.250 kg H_2O?

24. Determine the number of grams of solute needed to make each of the following molal solutions:
a. a 4.50 *m* solution of H_2SO_4 in 1.00 kg H_2O
b. a 1.00 *m* solution of HNO_3 in 2.00 kg H_2O

25. A solution is prepared by dissolving 17.1 g of sucrose, $C_{12}H_{22}O_{11}$, in 275 g of H_2O.
a. What is the molar mass of sucrose?
b. What is the molality of that solution?

26. How many kilograms of H_2O must be added to 75.5 g of $Ca(NO_3)_2$ to form a 0.500 *m* solution?

27. A solution made from ethanol, C_2H_5OH, and water is 1.75 *m*. How many grams of C_2H_5OH are contained per 250. g of water?

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MIXED REVIEW

28. Na_2SO_4 is dissolved in water to make 450 mL of a 0.250 M solution.
a. What is the molar mass of Na_2SO_4?
b. How many moles of Na_2SO_4 are needed?

29. Citric acid is one component of some soft drinks. Suppose that a 2 L solution is made from 150 mg of citric acid, $C_6H_8O_7$.
a. What is the molar mass of citric acid?
b. What products are produced once the soft drink is opened?
c. Would increasing the concentration of citric acid decrease the bubbling?
d. What is the molarity of citric acid in the solution?

30. Suppose you wanted to know how many grams of KCl would be left if 350 mL of a 6.0 M KCl solution were evaporated to dryness.
a. What is the molar mass of KCl?
b. How would heating the solution affect the mass of KCl remaining?
c. How many grams of KCl would remain?

31. Sodium metal reacts violently with water to form NaOH and release hydrogen gas. Suppose that 10.0 g of Na react completely with 1.00 L of water, and the final volume of the system is 1 L.
a. What is the molar mass of NaOH?
b. Write a balanced equation for the reaction.
c. What is the molarity of the NaOH solution formed by the reaction?

32. In cars, ethylene glycol, $C_2H_6O_2$, is used as a coolant and antifreeze. A mechanic fills a radiator with 6.5 kg of ethylene glycol and 1.5 kg of water.
a. What is the molar mass of ethylene glycol?
b. What is the molality of the water in the solution?

CRITICAL THINKING

33. Predicting Outcomes You have been investigating the nature of suspensions, colloids, and solutions and have collected the following observational data on four unknown samples. From the data, infer whether each sample is a solution, suspension, or colloid.

DATA TABLE 1 — SAMPLES

Sample	Color	Clarity (clear or cloudy)	Settle out	Tyndall effect
1	green	clear	no	no
2	blue	cloudy	yes	no
3	colorless	clear	no	yes
4	white	clear	no	yes

DATA TABLE 2 — FILTRATE OF SAMPLES

Sample	Color	Clarity (clear or cloudy)	On filter paper	Tyndall effect
1	green	clear	nothing	no
2	blue	cloudy	gray solid	yes
3	colorless	cloudy	none	yes
4	white	clear	white solid	no

Based on your inferences in Data Table 1, you decide to conduct one more test of the particles. You filter the samples and then reexamine the filtrate. You obtain the data found in Data Table 2. Infer the classifications based on the data in Table 2.

TECHNOLOGY & LEARNING

34. Graphing Calculator Predicting Solubility from Tabular Data

The graphing calculator can run a program that estimates data such as solubility at a given temperature. Given solubility measurements for KCl, you will use the data to predict its solubility at 50°C. Begin by creating a table of data. Then the program will carry out an extrapolation. The last step will involve solubility predictions.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that after creating your lists, you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

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a. At what temperature would you expect the solubility to be 48.9 g/100 g SatdSoln?
b. At what temperature would you expect the solubility to be 59 g/100 g SatdSoln?
c. At what solubility would you expect the temperature to be 100° C?

HANDBOOK SEARCH

35. Review the information on alloys in the *Elements Handbook*.
a. Why is aluminum such an important component of alloys?
b. What metals make up bronze?
c. What metals make up brass?
d. What is steel?
e. What is the composition of the mixture called cast iron?

36. Table 5A of the *Elements Handbook* contains carbon monoxide concentration data expressed as parts per million (ppm). The OSHA (Occupational Safety and Health Administration) limit for worker exposure to CO is 200 ppm for an eight-hour period.
a. At what concentration do harmful effects occur in less than one hour?
b. By what factor does the concentration in item (a) exceed the maximum limit set by OSHA?

RESEARCH & WRITING

37. Find out about the chemistry of emulsifying agents. How do these substances affect the dissolution of immiscible substances such as oil and water? As part of your research on this topic, find out why eggs are an emulsifying agent for baking mixtures.

ALTERNATIVE ASSESSMENT

38. Make a comparison of the electrolyte concentration in various brands of sports drinks. Using the labeling information for sugar, calculate the molarity of sugar in each product or brand. Construct a poster to show the results of your analysis of the product labels.

39. Write a set of instructions on how to prepare a solution that is 1 M $CuSO_4$ using $CuSO_4 \cdot 5H_2O$ as the solute. How do the instructions differ if the solute is anhydrous $CuSO_4$? Your instructions should include a list of all materials needed.

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CHAPTER 14

Ions in Aqueous Solutions and Colligative Properties

These formations were made by the precipitation of ionic compounds from an aqueous solution.

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Compounds in Aqueous Solutions

SECTION 14-1

Objectives

- Write equations for the dissolution of soluble ionic compounds in water.
- Predict whether a precipitate will form when solutions of soluble ionic compounds are combined, and write net ionic equations for precipitation reactions.
- Compare dissociation of ionic compounds with ionization of molecular compounds.
- Draw the structure of the hydronium ion, and explain why it is used to represent the hydrogen ion in solution.
- Distinguish between strong electrolytes and weak electrolytes.

As you have learned, solid compounds can be ionic or molecular. In an ionic solid, a crystal structure is made up of charged particles held together by ionic attractions. In a molecular solid, molecules are composed of covalently bonded atoms held together by intermolecular forces. When they dissolve in water, ionic compounds and molecular compounds behave differently.

Dissociation

When a compound that is made of ions dissolves in water, the ions separate from one another, as shown in Figure 14-1. *This separation of ions that occurs when an ionic compound dissolves is called* **dissociation.** For example, dissociation of sodium chloride and calcium chloride in water can be represented by the following equations. (As usual, (*s*) indicates a solid species and (*aq*) indicates a species in an aqueous solution. Note that the equation is balanced for charge as well as for atoms.)

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

$$CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq)$$

Notice the number of ions produced per formula unit in the equations above. One formula unit of sodium chloride gives two ions in solution, whereas one formula unit of calcium chloride gives three ions in solution.

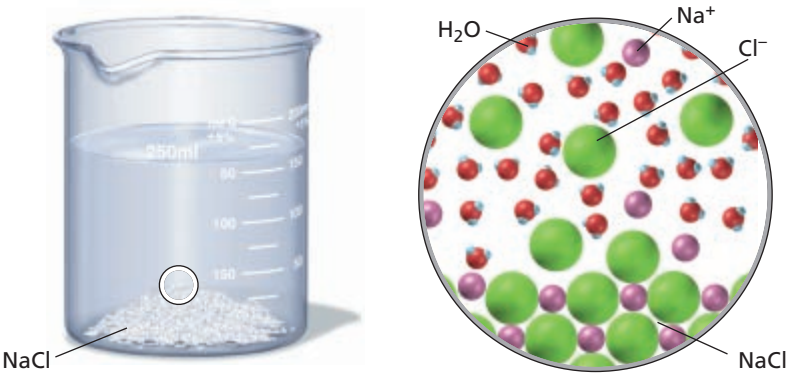

FIGURE 14-1 When NaCl dissolves in water, the ions separate as they leave the crystal.

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Assuming 100% dissociation, a solution that contains 1 mol of sodium chloride contains 1 mol of Na^+ ions and 1 mol of Cl^- ions. In this book, you can assume 100% dissociation for all soluble ionic compounds. The dissociation of NaCl can be represented as follows.

$$\underset{1\text{ mol}}{NaCl(s)} \xrightarrow{H_2O} \underset{1\text{ mol}}{Na^+(aq)} + \underset{1\text{ mol}}{Cl^-(aq)}$$

A solution that contains 1 mol of calcium chloride contains 1 mol of Ca^{2+} ions and 2 mol of Cl^- ions—a total of 3 mol of ions.

$$\underset{1\text{ mol}}{CaCl_2(s)} \xrightarrow{H_2O} \underset{1\text{ mol}}{Ca^{2+}(aq)} + \underset{2\text{ mol}}{2Cl^-(aq)}$$

SAMPLE PROBLEM 14-1

Write the equation for the dissolution of aluminum sulfate, $Al_2(SO_4)_3$, in water. How many moles of aluminum ions and sulfate ions are produced by dissolving 1 mol of aluminum sulfate? What is the total number of moles of ions produced by dissolving 1 mol of aluminum sulfate?

SOLUTION

1 ANALYZE

Given: amount of solute = 1 mol $Al_2(SO_4)_3$
solvent identity = water

Unknown: **a.** moles of aluminum ions and sulfate ions
b. total number of moles of solute ions produced

2 PLAN

The coefficients in the balanced dissociation equation will reveal the mole relationships, so you can use the equation to determine the number of moles of solute ions produced.

$$Al_2(SO_4)_3(s) \xrightarrow{H_2O} 2Al^{3+}(aq) + 3SO_4^{2-}(aq)$$

3 COMPUTE

a. 1 mol $Al_2(SO_4)_3 \rightarrow$ 2 mol Al^{3+} + 3 mol SO_4^{2-}
b. 2 mol Al^{3+} + 3 mol SO_4^{2-} = 5 mol of solute ions

4 EVALUATE

The equation is correctly balanced. Because one formula unit of $Al_2(SO_4)_3$ produces 5 ions, 1 mol of $Al_2(SO_4)_3$ produces 5 mol of ions.

PRACTICE

1. Write the equation for the dissolution of each of the following in water, and then determine the number of moles of each ion produced as well as the total number of moles of ions produced.
   a. 1 mol ammonium chloride
   b. 1 mol sodium sulfide
   c. 0.5 mol barium nitrate

Answer

a. $NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$;
1 mol NH_4^+, 1 mol Cl^-, 2 mol ions

b. $Na_2S(s) \xrightarrow{H_2O} 2Na^+(aq) + S^{2-}(aq)$;
2 mol Na^+, 1 mol S^{2-}, 3 mol ions

c. $Ba(NO_3)_2(s) \xrightarrow{H_2O} Ba^{2+}(aq) + 2NO_3^-(aq)$;
0.5 mol Ba^{2+}, 1 mol NO_3^-, 1.5 mol ions

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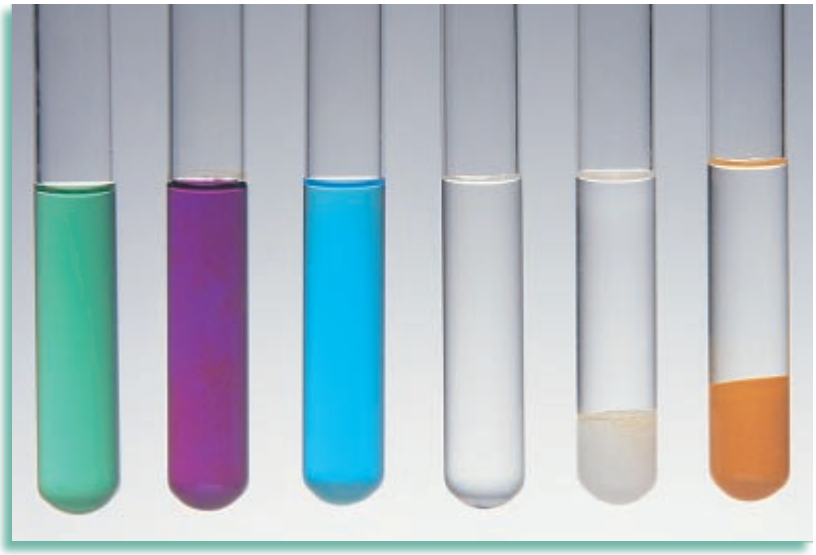

FIGURE 14-2 Ionic compounds can be soluble or insoluble in water. $NiCl_2$, $KMnO_4$, $CuSO_4$, and $Pb(NO_3)_2$ are soluble in water. AgCl and CdS are insoluble in water.

Precipitation Reactions

Although no compound is completely insoluble, compounds of very low solubility can be considered insoluble for most practical purposes. Some examples of ionic compounds that are soluble and insoluble in water are shown in Figure 14-2. It is difficult to write solubility rules that cover all possible conditions. However, we can write some general guidelines to help predict whether a compound made of a certain combination of ions is soluble. These general solubility guidelines are given in Table 14-1.

By looking at the table you can tell that most sodium compounds are soluble. Sodium carbonate, Na_2CO_3, is soluble because it contains sodium. Its dissociation equation is as follows.

$$Na_2CO_3(s) \xrightarrow{H_2O} 2Na^+(aq) + CO_3^{2-}(aq)$$

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TABLE 14-1 *General Solubility Guidelines*

1.	Most sodium, potassium, and ammonium compounds are soluble in water.
2.	Most nitrates, acetates, and chlorates are soluble.
3.	Most chlorides are soluble, except those of silver, mercury(I), and lead. Lead(II) chloride is soluble in hot water.
4.	Most sulfates are soluble, except those of barium, strontium, and lead.
5.	Most carbonates, phosphates, and silicates are insoluble, except those of sodium, potassium, and ammonium.
6.	Most sulfides are insoluble, except those of calcium, strontium, sodium, potassium, and ammonium.

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Is calcium phosphate, $Ca_3(PO_4)_2$, soluble or insoluble? According to Table 14-1, most phosphates are insoluble. Calcium phosphate is not one of the exceptions listed, so it is insoluble. Dissociation equations cannot be written for insoluble compounds.

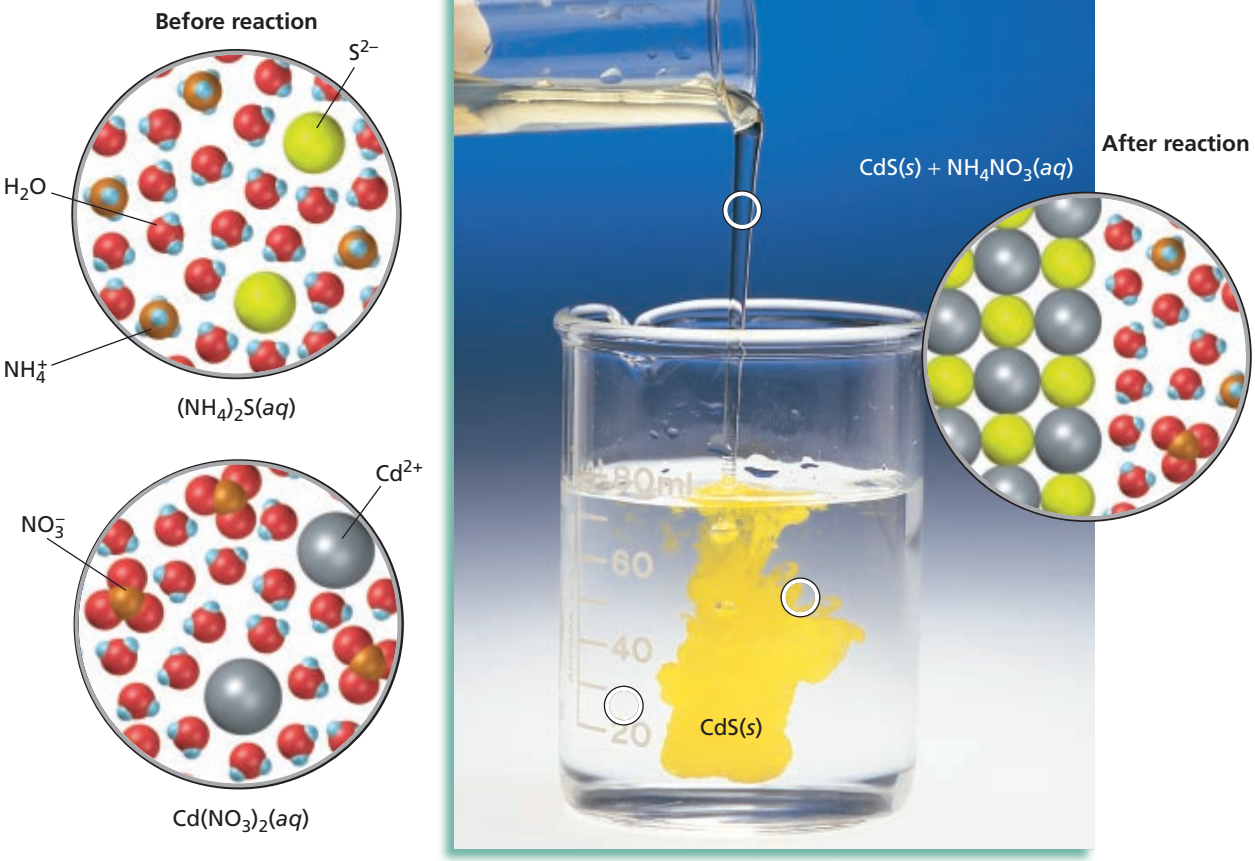
The information in Table 14-1 is also useful in predicting what will happen if solutions of two different soluble compounds are mixed. If the mixing results in a combination of ions that forms an insoluble compound, a double-replacement reaction and precipitation will occur. Precipitation occurs because the attraction between the ions is greater than the attraction between the ions and surrounding water molecules.

Will a precipitate form when solutions of ammonium sulfide and cadmium nitrate are combined? By using the table, you can tell that cadmium nitrate, $Cd(NO_3)_2$, is soluble because it is a nitrate and all nitrates are soluble. You can also tell that ammonium sulfide, $(NH_4)_2S$, is soluble. It is one of the sulfides listed in the table as being soluble. Their dissociation equations are as follows.

$$(NH_4)_2S(s) \xrightarrow{H_2O} 2NH_4^+(aq) + S^{2-}(aq)$$

$$Cd(NO_3)_2(s) \xrightarrow{H_2O} Cd^{2+}(aq) + 2NO_3^-(aq)$$

FIGURE 14-3 Ammonium sulfide is a soluble compound that dissociates in water to form NH_4^+ and S^{2-} ions. Cadmium nitrate is a soluble compound that dissociates in water to form NO_3^- and Cd^{2+} ions. Precipitation of cadmium sulfide occurs when the two solutions are mixed.



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The two possible products of a double-replacement reaction between $(NH_4)_2S$ and $Cd(NO_3)_2$ are ammonium nitrate, NH_4NO_3, and cadmium sulfide, CdS. (The question marks indicate that the states are unknown.)

$$(NH_4)_2S(aq) + Cd(NO_3)_2(aq) \longrightarrow NH_4NO_3(?) + CdS(?)$$

To decide whether a precipitate can form, you must know the solubilities of these two compounds. Consulting Table 14-1, you can see that NH_4NO_3 is soluble in water. However, CdS is insoluble. You can therefore predict that when solutions of ammonium sulfide and cadmium nitrate are combined, ammonium nitrate will not precipitate and cadmium sulfide will. As illustrated in Figure 14-3, crystals of CdS form when the solutions are mixed. In the following equation, the designations (*aq*) and (*s*) show that ammonium nitrate remains in solution and cadmium sulfide precipitates.

$$(NH_4)_2S(aq) + Cd(NO_3)_2(aq) \longrightarrow NH_4NO_3(aq) + CdS(s)$$

Net Ionic Equations

Reactions of ions in aqueous solution are usually represented by net ionic equations rather than formula equations. *A* **net ionic equation** *includes only those compounds and ions that undergo a chemical change in a reaction in an aqueous solution.* To write a net ionic equation, you first convert the chemical equation into an overall ionic equation. All soluble ionic compounds are shown as dissociated ions in solution. The precipitates are shown as solids. The precipitation of cadmium sulfide described previously can be shown by the following overall ionic equation.

$$Cd^{2+}(aq) + 2NO_3^-(aq) + 2NH_4^+(aq) + S^{2-}(aq) \longrightarrow CdS(s) + 2NO_3^-(aq) + 2NH_4^+(aq)$$

Notice that the ammonium ion, NH_4^+, and the nitrate ion, NO_3^-, appear on both sides of this equation. Therefore, they have not undergone any chemical change and are still present in their original form. *Ions that do not take part in a chemical reaction and are found in solution both before and after the reaction are* **spectator ions.**

To convert an ionic equation into a net ionic equation, the spectator ions are canceled on both sides of the equation. Eliminating the NH_4^+ and NO_3^- ions from the overall ionic equation above gives the following net ionic equation.

$$Cd^{2+}(aq) + S^{2-}(aq) \longrightarrow CdS(s)$$

This net ionic equation applies not only to the reaction between $(NH_4)_2S$ and $Cd(NO_3)_2$ but also to *any* reaction in which a precipitate of cadmium sulfide forms when the ions are combined in solution. For example, it is also the net ionic equation for the precipitation of CdS when $CdSO_4$ and H_2S react.

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SAMPLE PROBLEM 14-2

Identify the precipitate that forms when aqueous solutions of zinc nitrate and ammonium sulfide are combined. Write the equation for the possible double-replacement reaction. Then write the formula equation, overall ionic equation, and net ionic equation for the reaction.

SOLUTION

1 ANALYZE

Given: identity of reactants: zinc nitrate and ammonium sulfide
reaction medium: aqueous solution

Unknown: **a.** equation for the possible double-replacement reaction **b.** identity of the precipitate **c.** formula equation **d.** overall ionic equation **e.** net ionic equation

2 PLAN

Write the possible double-replacement reaction between $Zn(NO_3)_2$ and $(NH_4)_2S$. Use Table 14-1 to determine if any of the products are insoluble and will precipitate. Write a formula equation and an overall ionic equation, then cancel the spectator ions to produce a net ionic equation.

3 COMPUTE

a. The equation for the possible double-replacement reaction is as follows.

$$Zn(NO_3)_2(aq) + (NH_4)_2S(aq) \longrightarrow ZnS(?) + 2NH_4NO_3(?)$$

b. Table 14-1 reveals that zinc sulfide is not a soluble sulfide and is therefore a precipitate. Ammonium nitrate is soluble according to the table.

c. The formula equation is as follows.

$$Zn(NO_3)_2(aq) + (NH_4)_2S(aq) \longrightarrow ZnS(s) + 2NH_4NO_3(aq)$$

d. The overall ionic equation is as follows.

$$Zn^{2+}(aq) + 2NO_3^-(aq) + 2NH_4^+(aq) + S^{2-}(aq) \longrightarrow ZnS(s) + 2NH_4^+(aq) + 2NO_3^-(aq)$$

e. The ammonium and nitrate ions appear on both sides of the equation as spectator ions. The net ionic equation is as follows.

$$Zn^{2+}(aq) + S^{2-}(aq) \longrightarrow ZnS(s)$$

PRACTICE

1. Will a precipitate form if solutions of potassium sulfate and barium nitrate are combined? If so, write the net ionic equation for the reaction.

   Answer
   Yes;
   $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

2. Will a precipitate form if solutions of potassium nitrate and magnesium sulfate are combined? If so, write the net ionic equation for the reaction.

   Answer
   No

3. Will a precipitate form if solutions of barium chloride and sodium sulfate are combined? If so, identify the spectator ions and write the net ionic equation.

   Answer
   Yes; Na^+ and Cl^-;
   $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

4. Write the net ionic equation for the precipitation of nickel(II) sulfide.

   Answer
   $Ni^{2+}(aq) + S^{2-}(aq) \longrightarrow NiS(s)$

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Ionization

Some molecular compounds can also form ions in solution. Usually such compounds are polar. *Ions are formed from solute molecules by the action of the solvent in a process called* **ionization.** The more general meaning of this term is the creation of ions where there were none. Note that *ionization* is different from *dissociation*. When an ionic compound dissolves, the ions that were already present separate from one another. When a molecular compound dissolves and ionizes in a polar solvent, ions are formed where none existed in the undissolved compound. Like all ions in aqueous solution, the ions formed by such a molecular solute are hydrated. The heat released during the hydration of the ions provides the energy needed to break the covalent bonds.

In general, the extent to which a solute ionizes in solution depends on the strength of the bonds within the molecules of the solute and the strength of attraction between the solute and solvent molecules. If the strength of a bond within the solute molecule is weaker than the attractive forces of the solvent molecules, then the covalent bond of the solute breaks and the molecule is separated into ions. Hydrogen chloride, HCl, is a molecular compound that ionizes in aqueous solution. It contains a highly polar bond. The attraction between a polar HCl molecule and the polar water molecules is strong enough to break the HCl bond, forming hydrogen ions and chloride ions.

$$HCl \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

The Hydronium Ion

The H^+ ion attracts other molecules or ions so strongly that it does not normally exist alone. The ionization of hydrogen chloride in water is better described as a chemical reaction in which a proton is transferred directly from HCl to a water molecule, where it becomes covalently bonded to oxygen and forms H_3O^+.

$$H_2O(l) + HCl(g) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

This process is represented in Figure 14-4. *The H_3O^+ ion is known as the* **hydronium ion.**

The hydration of the H^+ ion to form the hydronium ion is a highly exothermic reaction. The energy released makes a large contribution to the energy needed to ionize a molecular solute. Many molecular compounds that ionize in an aqueous solution contain hydrogen and form H_3O^+.

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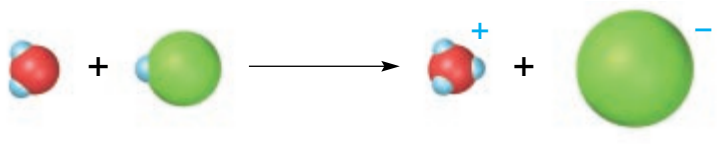

FIGURE 14-4 When hydrogen chloride gas dissolves in water, it ionizes to form an H^+ ion and a Cl^- ion. The H^+ ion immediately bonds to a water molecule, forming a hydronium ion. The aqueous solution of hydrogen chloride is called hydrochloric acid.

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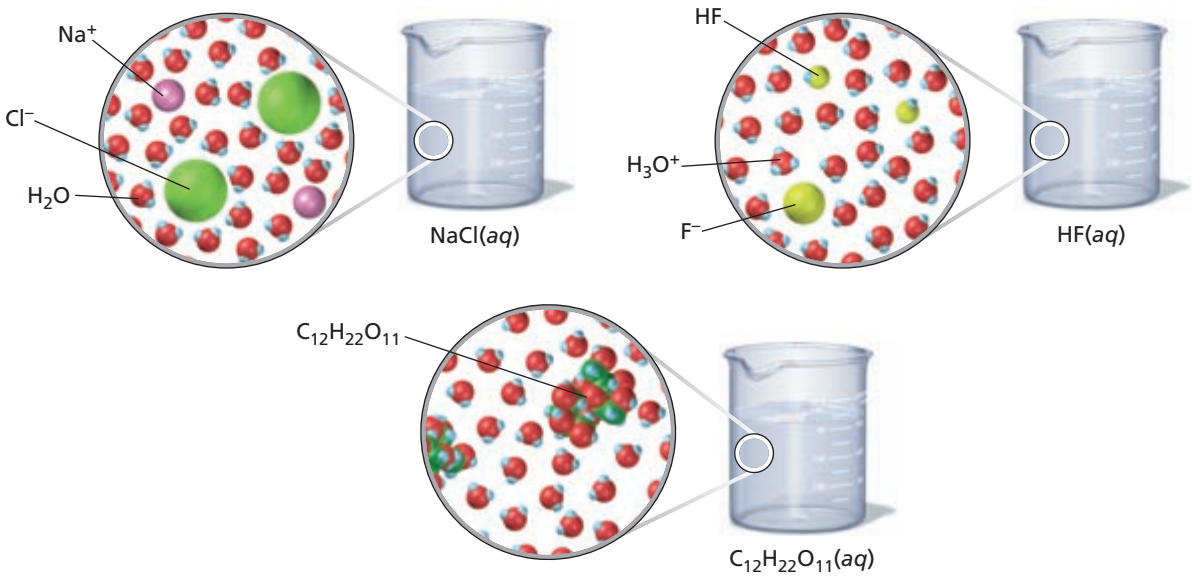

FIGURE 14-5 Strong electrolytes, such as NaCl, yield only ions when they dissolve in aqueous solution. Weak electrolytes, such as HF, exist as both ions and unionized molecules in aqueous solution. Nonelectrolytes, such as sucrose, $C_{12}H_{22}O_{11}$, do not form any ions in aqueous solution.

Strong and Weak Electrolytes

As discussed in Chapter 13, substances that yield ions and conduct an electric current in solution are electrolytes. Substances that do not yield ions and do not conduct an electric current in solution are nonelectrolytes. Hydrogen chloride is one of a series of compounds composed of hydrogen and the members of Group 17 (known as the halogens). The hydrogen halides are all molecular compounds with single polar-covalent bonds. All are gases, all are very soluble in water, and all are electrolytes. Hydrogen chloride, hydrogen bromide, and hydrogen iodide strongly conduct an electric current in an aqueous solution. However, hydrogen fluoride only weakly conducts an electric current at the same concentration. The strength with which substances conduct an electric current is related to their ability to form ions in solution, as shown in Figure 14-5.

CHEMISTRY INTERACTIVE TUTOR

Module 8: Strong and Weakly Ionized Species, pH, and Titrations

Strong Electrolytes

Hydrogen chloride, hydrogen bromide, and hydrogen iodide are 100% ionized in dilute aqueous solution. A **strong electrolyte** *is any compound whose dilute aqueous solutions conduct electricity well; this is due to the presence of all or almost all of the dissolved compound in the form of ions.* Hydrogen chloride, hydrogen bromide, and hydrogen iodide are all acids in aqueous solution. These acids, several other acids, and all soluble ionic compounds are strong electrolytes.

The distinguishing feature of strong electrolytes is that, to whatever extent they dissolve in water, they yield only ions. For example, an ionic compound may be highly soluble in water and dissociate into ions in solution, such as NaCl. Other ionic compounds may not dissolve much,

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but the amount that does dissolve exists solely as hydrated ions in solution.

Weak Electrolytes

An aqueous solution of some molecular compounds contains not only dissolved ions but also some dissolved molecules that are not ionized. Hydrogen fluoride, HF, dissolves in water to give an acid solution known as hydrofluoric acid. However, the hydrogen-fluorine bond is much stronger than the bonds between hydrogen and the other halogens. When hydrogen fluoride dissolves, some molecules ionize. But the reverse reaction—the transfer of H^+ ions back to F^- ions to form hydrogen fluoride molecules—also takes place.

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Thus, the concentration of dissolved unionized HF molecules remains high and the concentration of H_3O^+ and F^- ions remains low.

Hydrogen fluoride is an example of a *weak electrolyte. A* **weak electrolyte** *is any compound whose dilute aqueous solutions conduct electricity poorly; this is due to the presence of a small amount of the dissolved compound in the form of ions.* This is in contrast to a nonelectrolyte, of which none of the dissolved compound exists as ions. Another example of a weak electrolyte is acetic acid, CH_3COOH. Only a small percentage of the acetic acid molecules ionize in aqueous solution.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

The description of an electrolyte as strong or weak must not be confused with the description of a solution as concentrated or dilute. Strong and weak electrolytes differ in the *degree of ionization or dissociation.* Concentrated and dilute solutions differ in the *amount of solute dissolved* in a given quantity of a solvent. Hydrochloric acid is always a strong electrolyte. This is true even in a solution that is 0.000 01 M—a very dilute solution. By contrast, acetic acid is always considered a weak electrolyte, even in a 10 M solution—a fairly concentrated solution.

SECTION REVIEW

1. Write the equation for the dissolution of $Sr(NO_3)_2$ in water. How many moles of strontium ions and nitrate ions are produced by dissolving 0.5 mol of strontium nitrate?
2. Will a precipitate form if solutions of magnesium acetate and strontium chloride are combined?
3. What determines whether a molecular compound will be ionized in a polar solvent?
4. How is a hydronium ion formed when a compound like HCl dissolves in water? What is its net charge?
5. Explain why HCl is a strong electrolyte and HF is a weak electrolyte.

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The Riddle of Electrolysis

HISTORICAL PERSPECTIVE

When Michael Faraday performed his electrochemical experiments, little was known about the relationship between matter and electricity. Chemists were still debating the existence of atoms, and the discovery of the electron was more than 50 years away. Combining his talents in electrical and chemical investigation, Faraday pointed researchers to the intimate connection between chemical reactions and electricity while setting the stage for the development of a new branch of chemistry.

Chlorine being produced by electrolysis.

Electrifying Experiments

In 1800, the Italian physicist Alessandro Volta introduced his "voltaic pile," better known as the battery. The stack of alternating zinc and silver disks provided scientists with a source of electric current for the first time, and, in the words of the famous English chemist Humphry Davy, it acted as "an alarm-bell to experimenters in every part of Europe."

That same year, chemists discovered a new phenomenon using Volta's device. They immersed the two poles of a battery at different locations in a container of water. As current flowed, the water decomposed into its elemental components, with hydrogen evolving at the positive pole of the battery and oxygen evolving at the negative pole. Similar experiments using solutions of certain solids dissolved in water resulted in the decomposition of the solids, with the two products of their breakdown also evolving at opposite poles of the battery. This electrochemical decomposition was later named electrolysis.

The Roots of Electrolytic Theory

The discovery of electrolysis led two pioneering chemists to ponder the connection between chemical forces and electricity. One of them was Davy:

> *Is not what has been called chemical affinity merely the union . . . of particles in naturally opposite states? And are not chemical attractions of particles and electrical attractions of masses owing to one property and governed by one simple law?*

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The Swedish chemist Jöns Jacob Berzelius took Davy's idea a step further. He postulated that matter consisted of combinations of "electropositive" and "electronegative" substances, classifying the parts by the pole at which they accumulated during electrolysis.

These ideas inspired two early electrolytic theories, each of which ultimately proved incorrect but which contributed to our present understanding of the phenomenon. The "contact theory" proposed that electrolytic current was due merely to the contact of the battery's metals with the electrolytic solution. The "chemical theory," on the other hand, attributed the flow of current to undefined changes in the solution's components.

Faraday Provides a Spark

Although Michael Faraday is best remembered for his work in electromagnetism, he began his career as Humphry Davy's laboratory assistant at the Royal Institution, in London, and went on to be the professor of chemistry there for over 30 years. In the 1830s, Faraday devised several ingenious experiments to determine whether the flow of current in an electrolytic solution is dependent solely on the contact of the battery's poles with the solution. In a typical setup, one of the poles was separated from the solution and electricity was permitted to enter it by way of a spark. In all cases, Faraday observed current to flow in the electrolytic cell despite one or both of the poles not being in direct contact with the electrolytic solution. In 1833 he wrote the following:

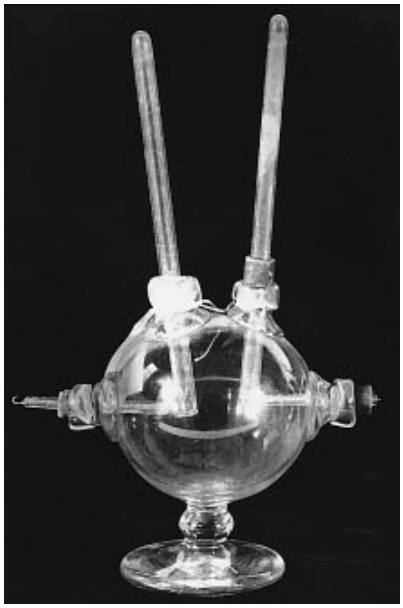
> *I conceive the effects [of electrolysis] to arise from forces which are* internal, *relative to the matter under decomposition, and not* external, *as they might be considered, if directly dependent on the poles. I suppose that the effects are due to a modification, by the electric current, of the chemical affinity of the particles through or by which the current is passing.*

Although the battery's poles were, in fact, later shown to play a part in the flow of the current, Faraday had established the active role of the electrolytic solution in electrolysis. And in realizing that electricity affected the chemical nature of the solution, he anticipated the ideas of oxidation and reduction—despite the fact that the concepts of electrons and ions were half a century away.

Faraday's Legacy

Faraday continued to study the role of the electrolytic solution, or *electrolyte,* as he named it, in electrolysis. (He also coined most of the other modern terms of electrolysis, for example, *electrode, ion, anode, cathode, anion,* and *cation.*) These investigations culminated in the discovery of his basic laws of electrolysis.

Still valid today, these principles not only put electrolysis on a quantitative footing, leading to our current understanding of the phenomenon, but also bolstered the atomic theory, which was still seriously contested by many chemists at the time. And perhaps most important, Faraday's experiments inspired his successors to further clarify the chemical nature of solutions. This ultimately led to Svante Arrhenius's theory of electrolytic dissociation and the evolution of a new division in the chemical field, known today as physical chemistry.



Instrument used by Michael Faraday in his studies of electrolysis.

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SECTION 14-2

Colligative Properties of Solutions

Objectives

- List four colligative properties, and explain why they are classified as colligative properties.
- Calculate freezing-point depression, boiling-point elevation, and solution molality of nonelectrolytic solutions.
- Calculate the expected changes in freezing point and boiling point of an electrolytic solution.
- Discuss causes of the differences between expected and experimentally observed colligative properties of electrolytic solutions.

The presence of solutes affects the properties of the solutions. Some of these properties are not dependent on the nature of the dissolved substance but only on how many dissolved particles are present. *Properties that depend on the concentration of solute particles but not on their identity are called* **colligative properties.** In calculations involving some colligative properties, the concentration is given in terms of molality, *m*.

Vapor-Pressure Lowering

The boiling point and freezing point of a solution differ from those of the pure solvent. The graph in Figure 14-6 shows that a nonvolatile solute raises the boiling point and lowers the freezing point. *A* **nonvolatile substance** *is one that has little tendency to become a gas under existing conditions.*

Vapor Pressure vs. Temperature for a Pure Solvent and a Solution with a Nonvolatile Solute

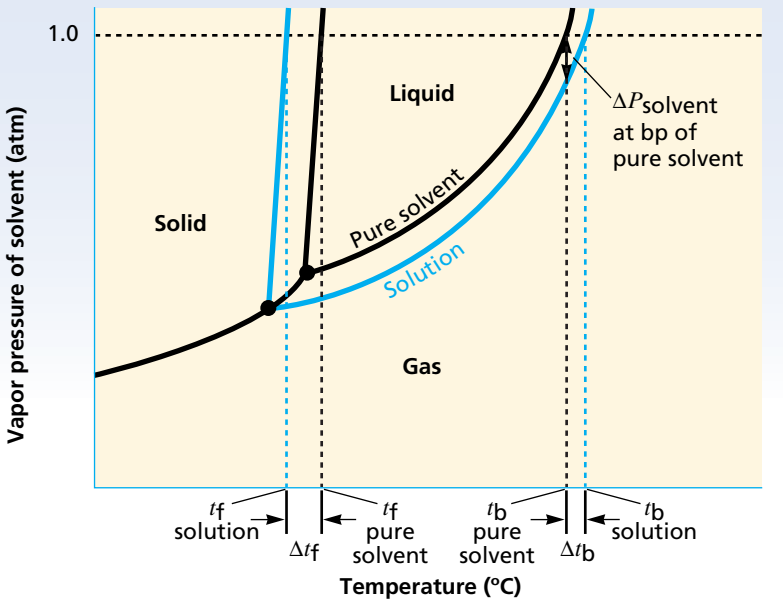

FIGURE 14-6 Vapor pressure as a function of temperature is shown for a pure solvent, a solution of that solvent, and a nonvolatile solute. The vapor pressure of the solution is lower than the vapor pressure of the pure solvent. (This can be seen by noting the decrease in pressure between the pure solvent and the solution at the temperature that is the boiling point of the pure solvent.) The solute thus reduces the freezing point and elevates the boiling point.

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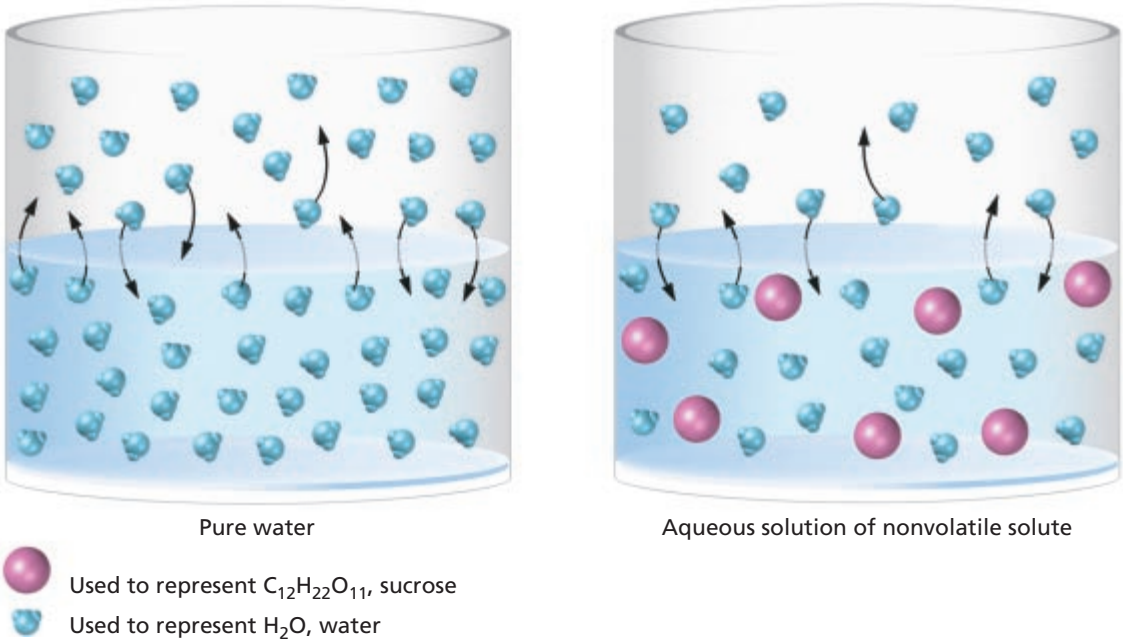

FIGURE 14-7 The vapor pressure of water over pure water is greater than the vapor pressure of water over an aqueous solution containing a nonvolatile solute, such as sucrose.

To understand why a nonvolatile solute changes the boiling point and freezing point, you must consider equilibrium vapor pressure, which was discussed in Chapter 12. Vapor pressure is the pressure caused by molecules that have escaped from the liquid phase to the gaseous phase. Experiments show that the vapor pressure of a solvent containing a nonvolatile solute is lower than the vapor pressure of the pure solvent at the same temperature, as shown in Figure 14-7. Notice the liquid-vapor boundaries. Vapor pressure can be thought of as a measure of the tendency of molecules to escape from a liquid. Addition of sucrose, a nonvolatile solute, lowers the concentration of water molecules at the surface of the liquid. This lowers the tendency of water molecules to leave the solution and enter the vapor phase. Thus, the vapor pressure of the solution is lower than the vapor pressure of pure water.

Nonelectrolyte solutions of the same molality have the same concentration of particles. Dilute solutions of the same solvent and equal molality of any nonelectrolyte solute lower vapor pressure equally. For example, a 1 *m* aqueous solution of the nonelectrolyte glucose, $C_6H_{12}O_6$, lowers the vapor pressure of water 5.5×10^{-4} atm at 25°C. A 1 *m* solution of sucrose, $C_{12}H_{22}O_{11}$, another nonelectrolyte, also lowers the vapor pressure 5.5×10^{-4} atm. Because vapor-pressure lowering depends on the concentration of a nonelectrolyte solute and is independent of solute identity, it is a colligative property.

Refer to the graph in Figure 14-6. Because the vapor pressure has been lowered, the solution remains liquid over a larger temperature range. This lowers the freezing point and raises the boiling point. It follows that changes in boiling point and freezing point also depend on the concentration of solute and are therefore colligative properties.

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Freezing-Point Depression

The freezing point of a 1-molal solution of any nonelectrolyte solute in water is found by experiment to be 1.86°C lower than the freezing point of water. That is, when 1 mol of a nonelectrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is –1.86°C instead of 0.00°C. When 2 mol of a nonelectrolyte solute is dissolved in 1 kg of water, the freezing point of the solution is –3.72°C. This is 2 × –1.86°C. In fact, for any concentration of a nonelectrolyte solute in water, the decrease in freezing point can be determined by using the value of –1.86°C/*m*. This value, called the **molal freezing-point constant (K_f),** *is the freezing-point depression of the solvent in a 1-molal solution of a nonvolatile, nonelectrolyte solute.*

Each solvent has its own characteristic molal freezing-point constant. The values of K_f for some common solvents are given in Table 14-2. These values are most accurate for dilute solutions at 1 atmosphere of pressure. Some variations are introduced in the value of K_f at other pressures and with more-concentrated solutions. The table also shows the values of a related quantity called K_b, which you will study next.

As stated earlier, the freezing point of a solution containing 1 mol of a nonelectrolyte solute in water is 1.86°C lower than the normal freezing point of water. *The* **freezing-point depression,** Δt_f, *is the difference between the freezing points of the pure solvent and a solution of a nonelectrolyte in that solvent, and it is directly proportional to the molal concentration of the solution.* As shown by the previous example, if the molal concentration is doubled, the freezing-point depression is doubled. Freezing-point depression can be calculated by the following equation.

$$\Delta t_f = K_f m$$

K_f is expressed as °C/*m*, *m* is expressed in mol solute/kg solvent (molality), and Δt_f is expressed in °C. Sample Problems 14-3 and 14-4 show how this relationship can be used to determine the freezing-point depression and molal concentration of a solution.

TABLE 14-2 *Molal Freezing-Point and Boiling-Point Constants*

Solvent	Normal f.p. (°C)	Molal f.p. constant, K_f (°C/*m*)	Normal b.p. (°C)	Molal b.p. constant, K_b (°C/*m*)
Acetic acid	16.6	–3.90	117.9	3.07
Camphor	178.8	–39.7	207.4	5.61
Ether	–116.3	–1.79	34.6	2.02
Naphthalene	80.2	–6.94	217.7	5.80
Phenol	40.9	–7.40	181.8	3.60
Water	0.00	–1.86	100.0	0.51

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SAMPLE PROBLEM 14-3

What is the freezing-point depression of water in a solution of 17.1 g of sucrose, $C_{12}H_{22}O_{11}$, and 200. g of water? What is the actual freezing point of the solution?

SOLUTION

1 ANALYZE

Given: solute mass and chemical formula = 17.1 g $C_{12}H_{22}O_{11}$
solvent mass and identity = 200.0 g water

Unknown: **a.** freezing-point depression
b. freezing point of the solution

2 PLAN

Find the molal freezing-point constant, K_f, for water in Table 14-2. To use the equation for freezing-point depression, $\Delta t_f = K_f m$, you need to determine the molality of the solution.

$$\text{mass of solute (g)} \times \frac{1 \text{ mol solute}}{\text{molar mass of solute (g)}} = \text{amount of solute (mol)}$$

$$\frac{\text{amount of solute (mol)}}{\text{mass of solvent (g)}} \times \frac{1000 \text{ g water}}{1 \text{ kg water}} = \text{molality}$$

$$\Delta t_f = K_f m$$

$$\text{f.p. solution} = \text{f.p. solvent} + \Delta t_f$$

3 COMPUTE

$$17.1 \cancel{\text{ g } C_{12}H_{22}O_{11}} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.34 \cancel{\text{ g } C_{12}H_{22}O_{11}}} = 0.0500 \text{ mol } C_{12}H_{22}O_{11}$$

$$\frac{0.0500 \text{ mol } C_{12}H_{22}O_{11}}{200. \cancel{\text{ g water}}} \times \frac{1000 \cancel{\text{ g water}}}{\text{kg water}} = \frac{0.250 \text{ mol } C_{12}H_{22}O_{11}}{\text{kg water}} = 0.250\ m$$

a. $\Delta t_f = 0.250 \cancel{m} \times (-1.86°\text{C}/\cancel{m}) = -0.465°\text{C}$

b. f.p. solution = 0.000°C + (−0.465°C) = −0.465°C

SAMPLE PROBLEM 14-4

A water solution containing an unknown quantity of a nonelectrolyte solute is found to have a freezing point of −0.23°C. What is the molal concentration of the solution?

SOLUTION

1 ANALYZE

Given: freezing point of solution = −0.23°C

Unknown: molality of the solution

2 PLAN

Water is the solvent, so you will need the value of K_f, the molal-freezing-point constant for water, from Table 14-2. The Δt_f for this solution is the difference between the f.p. of water and the f.p. of the solution. Use the equation for freezing-point depression to calculate molality.

$$\Delta t_f = \text{f.p. of solution} - \text{f.p. of pure solvent}$$

$\Delta t_f = K_f m$ Solve for molality, m.

$$m = \frac{\Delta t_f}{K_f}$$

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3 COMPUTE

$$\Delta t_f = -0.23°C - 0.00°C = -0.23°C$$

$$m = \frac{-0.23°\cancel{C}}{-1.86°\cancel{C}/m} = 0.12\ m$$

4 EVALUATE

As shown by the unit cancellation, the answer gives the molality, as desired. The answer is properly limited to two significant digits.

PRACTICE

1. A solution consists of 10.3 g of the nonelectrolyte glucose, $C_6H_{12}O_6$, dissolved in 250. g of water. What is the freezing-point depression of the solution?

   Answer
   $-0.426°C$

2. In a laboratory experiment, the freezing point of an aqueous solution of glucose is found to be $-0.325°C$. What is the molal concentration of this solution?

   Answer
   0.175 *m*

3. If 0.500 mol of a nonelectrolyte solute are dissolved in 500.0 g of ether, what is the freezing point of the solution?

   Answer
   $-118.1°C$

4. The freezing point of an aqueous solution that contains a nonelectrolyte is $-9.0°C$.
   a. What is the freezing-point depression of the solution?
   b. What is the molal concentration of the solution?

   Answer
   a. $-9.0°C$
   b. 4.8 *m*

Boiling-Point Elevation

As you learned in Chapter 12, the boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the prevailing atmospheric pressure. Therefore, a change in the vapor pressure of the liquid will cause a corresponding change in the boiling point. As stated earlier, the vapor pressure of a solution containing a nonvolatile solute is lower than the vapor pressure of the pure solvent. This means that more heat will be required to raise the vapor pressure of the solution to equal the atmospheric pressure. Thus, the boiling point of a solution is higher than the boiling point of the pure solvent.

The **molal boiling-point constant** (K_b) *is the boiling-point elevation of the solvent in a 1-molal solution of a nonvolatile, nonelectrolyte solute.* The boiling-point elevation of a 1-molal solution of any nonelectrolyte solute in water has been found by experiment to be 0.51°C. Thus, the molal boiling-point constant for water is 0.51°C/*m*.

For different solvents, the boiling-point elevations of 1-molal solutions have different values. Some other values for K_b are included in Table 14-2. Like the freezing-point constants, these values are most accurate for dilute solutions.

The **boiling-point elevation,** Δt_b, *is the difference between the boiling points of the pure solvent and a nonelectrolyte solution of that solvent,*

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and it is directly proportional to the molal concentration of the solution.
Boiling-point elevation can be calculated by the following equation.

$$\Delta t_b = K_b m$$

When Δt_b is expressed in °C/*m* and *m* is expressed in mol of solute/kg of solvent, Δt_b is the boiling-point elevation in °C.

SAMPLE PROBLEM 14-5

What is the boiling-point elevation of a solution made from 20.0 g of a nonelectrolyte solute and 400.0 g of water? The molar mass of the solute is 62.0 g.

SOLUTION

1 ANALYZE

Given: solute mass = 20.0 g
solute molar mass = 62.0 g
solvent mass and identity = 400.0 g of water
Unknown: boiling-point elevation

2 PLAN

Find the molal boiling-point constant, K_b, for water in Table 14-2. To use the equation for boiling-point elevation, $\Delta t_b = K_b m$, you need to determine the molality of the solution.

$$\text{mass of solute (g)} \times \frac{\text{1 mol solute}}{\text{molar mass of solute (g)}} = \text{amount of solute (mol)}$$

$$\frac{\text{amount of solute (mol)}}{\text{mass of solvent (g)}} \times \frac{\text{1000 g water}}{\text{1 kg water}} = \text{molality}$$

$$\Delta t_b = K_b m$$

3 COMPUTE

$$20.0 \text{ g of solute} \times \frac{\text{1 mol solute}}{62.0 \text{ g of solute}} = 0.323 \text{ mol of solute}$$

$$\frac{0.323 \text{ mol of solute}}{400.0 \text{ g water}} \times \frac{1000 \text{ g water}}{\text{1 kg water}} = 0.808 \frac{\text{mol solute}}{\text{kg water}} = 0.808\ m$$

$$\Delta t_b = 0.51°\text{C}/m \times 0.808\ m = 0.41°\text{C}$$

PRACTICE

1. A solution contains 50.0 g of sucrose, $C_{12}H_{22}O_{11}$, a nonelectrolyte, dissolved in 500.0 g of water. What is the boiling-point elevation? *Answer* 0.15°C
2. A solution contains 450.0 g of sucrose, $C_{12}H_{22}O_{11}$, a nonelectrolyte, dissolved in 250 g of water. What is the boiling point of the solution? *Answer* 102.7°C
3. If the boiling point elevation of an aqueous solution containing a nonvolatile electrolyte is 1.02°C, what is the molality of the solution? *Answer* 2.0 *m*
4. The boiling point of an aqueous solution containing a nonvolatile electrolyte is 100.75°C.
   a. What is the boiling-point elevation?
   b. What is the molality of the solution?
   Answer a. 0.75°C b. 1.5 *m*

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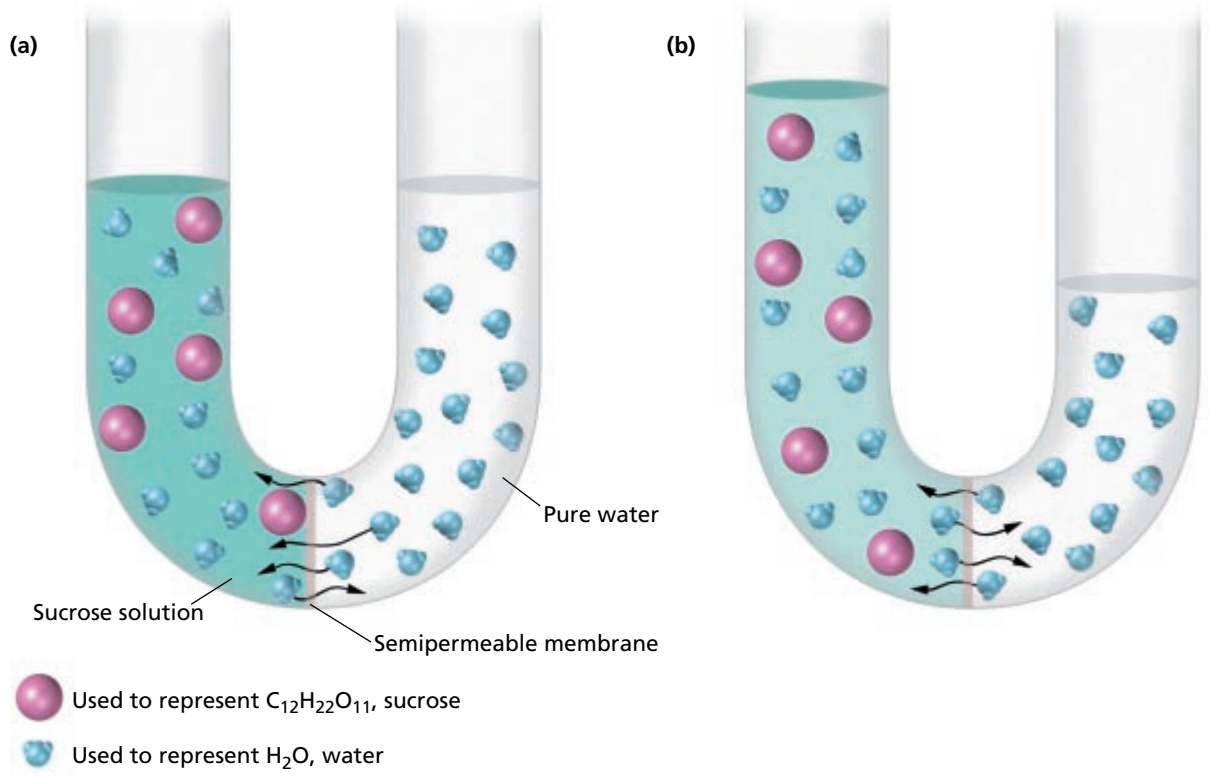

FIGURE 14-8 (a) When pure water and an aqueous sucrose solution are separated by a semipermeable membrane, the net movement of water molecules through the membrane is from the pure water side into the aqueous solution. (b) The level of the solution rises until pressure exerted by the height of the solution equals the osmotic pressure, at which point no net movement of water molecules occurs.

Osmotic Pressure

Figure 14-8 illustrates another colligative property. In the figure, an aqueous sucrose solution is separated from pure water by a semipermeable membrane. **Semipermeable membranes** *allow the movement of some particles while blocking the movement of others.* The level of the sucrose solution will rise until a certain height is reached. What causes the level of the solution to rise?

The semipermeable membrane allows water molecules, but not sucrose molecules, to pass through. The sucrose molecules on the solution side allow fewer water molecules to strike the membrane than strike on the pure water side in the same amount of time. Thus, the rate at which water molecules leave the pure water side is greater than the rate at which they leave the solution. This causes the level of the solution to rise. The level rises until the pressure exerted by the height of the solution is large enough to force water molecules back through the membrane from the solution at a rate equal to that at which they enter from the pure water side.

The movement of solvent through a semipermeable membrane from the side of lower solute concentration to the side of higher solute concentration is **osmosis.** Osmosis occurs whenever two solutions of different concentrations are separated by a semipermeable membrane. **Osmotic pressure** *is the external pressure that must be applied to stop osmosis.* In the example given above, osmosis caused the level of the solution to rise until the height of the solution provided the pressure necessary to stop osmosis. Because osmotic pressure is dependent on the concentration of

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solute particles and not on the type of solute particles, it is a colligative property. The greater the concentration of a solution, the greater the osmotic pressure of the solution.

Regulation of osmosis is vital to the life of a cell because cell membranes are semipermeable. Cells lose water and shrink when placed in a solution of higher concentration. They gain water and swell when placed in a solution of lower concentration. In vertebrates, cells are protected from swelling and shrinking by blood and lymph that surround the cells. Blood and lymph are equal in concentration to the concentration inside the cell.

Electrolytes and Colligative Properties

Early investigators were puzzled by experiments in which certain substances depressed the freezing point or elevated the boiling point of a solvent more than expected. For example, a 0.1 *m* solution of sodium chloride, NaCl, lowers the freezing point of the solvent nearly twice as much as a 0.1 *m* solution of sucrose. A 0.1 *m* solution of calcium chloride, $CaCl_2$, lowers the freezing point of the solvent nearly three times as much as a 0.1 *m* solution of sucrose. The effect on boiling points is similar.

To understand why this is so, contrast the behavior of sucrose with that of sodium chloride in aqueous solutions. Each sucrose molecule dissolves to produce only one particle in solution. So 1 mol of sucrose dissolves to produce only 1 mol of particles in solution. Sugar is a nonelectrolyte. NaCl, however, is a strong electrolyte. Each mole of NaCl dissolves to produce 2 mol of particles in solution: 1 mol of sodium ions and 1 mol of chloride ions. Figure 14-9 compares the production of particles in solution for three different solutes. As you can see, electrolytes produce more than 1 mol of solute particles for each mole of compound dissolved.

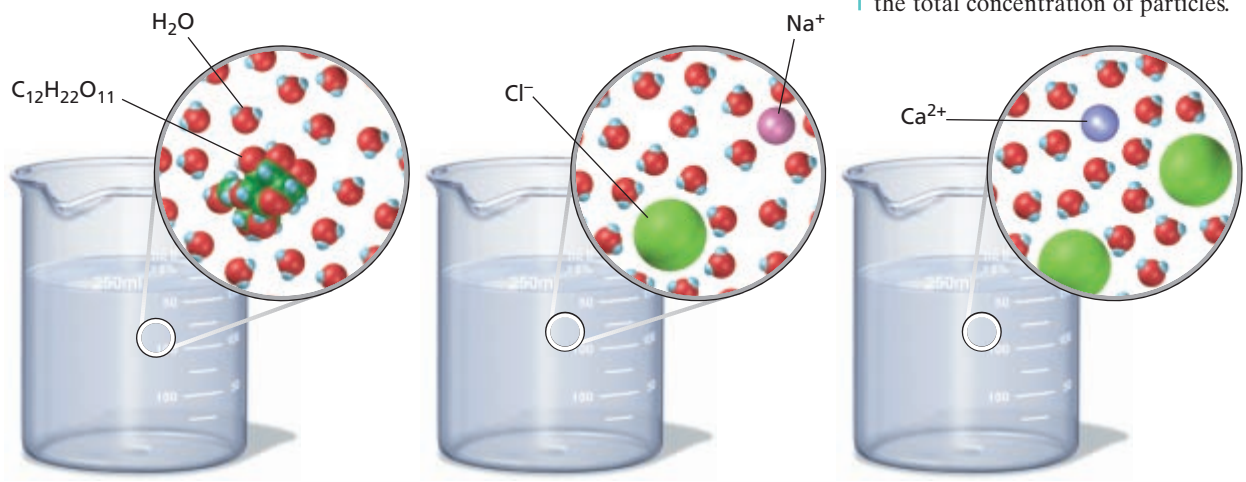

FIGURE 14-9 Compare the number of particles produced per formula unit for these three solutes. Colligative properties depend on the total concentration of particles.

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Calculated Values for Electrolyte Solutions

Remember that colligative properties depend on the total concentration of solute particles regardless of their identity. So electrolytes cause changes in colligative properties proportional to the total molality in terms of all dissolved particles instead of formula units. For the same molal concentrations of sucrose and sodium chloride, you would expect the effect on colligative properties to be twice as large for sodium chloride as for sucrose. What about barium nitrate, $Ba(NO_3)_2$? Each mole of barium nitrate yields 3 mol of ions in solution.

$$Ba(NO_3)_2(s) \longrightarrow Ba^{2+}(aq) + 2NO_3^-(aq)$$

You would expect a $Ba(NO_3)_2$ solution of a given molality to lower the freezing point of its solvent three times as much as a nonelectrolytic solution of the same molality.

SAMPLE PROBLEM 14-6

What is the expected change in the freezing point of water in a solution of 62.5 g of barium nitrate, $Ba(NO_3)_2$, in 1.00 kg of water?

SOLUTION

1 ANALYZE

Given: solute mass and formula = 62.5 g $Ba(NO_3)_2$
solvent mass and identity = 1.00 kg water
$\Delta t_f = K_f m$

Unknown: expected freezing-point depression

2 PLAN

The molality can be calculated by converting the solute mass to moles and then dividing by the number of kilograms of solvent. That molality is in terms of formula units of $Ba(NO_3)_2$ and must be converted to molality in terms of dissociated ions in solution. It must be multiplied by the number of moles of ions produced per mole of formula unit. This adjusted molality can then be used to calculate the freezing-point depression.

$$\frac{\text{mass of solute (g)}}{\text{mass of solvent (kg)}} \times \frac{\text{1 mol solute}}{\text{molar mass of solute (g)}} = \text{molality of solution}\left(\frac{\text{mol}}{\text{kg}}\right)$$

$$\text{molality of solution}\left(\frac{\text{mol}}{\text{kg}}\right) \times \text{molality conversion}\left(\frac{\text{mol ions}}{\text{mol}}\right) \times K_f\left(\frac{\text{°C} \cdot \text{kg } H_2O}{\text{mol ions}}\right)$$
$$= \text{expected freezing-point depression (°C)}$$

This problem is similar to Sample Problem 14-5, except that the solute is ionic rather than a nonionizing molecular solute. The number of particles in solution will therefore equal the number of ions of the solute.

3 COMPUTE

$$\frac{62.5 \text{ g } \cancel{Ba(NO_3)_2}}{1.00 \text{ kg } H_2O} \times \frac{\text{mol } Ba(NO_3)_2}{261.35 \text{ g } \cancel{Ba(NO_3)_2}} = \frac{0.239 \text{ mol } Ba(NO_3)_2}{\text{kg } H_2O}$$

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$$Ba(NO_3)_2(s) \longrightarrow Ba^{2+}(aq) + 2NO_3^-(aq)$$

Each formula unit of barium nitrate yields three ions in solution.

$$\frac{0.239 \text{ mol } Ba(NO_3)_2}{\text{kg } H_2O} \times \frac{3 \text{ mol ions}}{\text{mol } Ba(NO_3)_2} \times \frac{-1.86°C \cdot \text{kg } H_2O}{\text{mol ions}} = -1.33°C$$

4 EVALUATE

The units cancel properly to give the desired answer in °C. The answer is correctly given to three significant digits. The mass of the solute is approximately one-fourth its molar mass and would give 0.75 mol of ions in the 1 kg of solvent, so the estimated answer of $0.75 \times -1.86°C = -1.4°C$ supports our computation.

PRACTICE

1. What is the expected freezing-point depression for a solution that contains 2.0 mol of magnesium sulfate dissolved in 1.0 kg of water? *Answer* –7.4°C
2. What is the expected boiling-point elevation of water for a solution that contains 150 g of sodium chloride dissolved in 1.0 kg of water? *Answer* 2.7°C
3. The freezing point of an aqueous sodium chloride solution is –20.0°C. What is the molality of the solution? *Answer* 5.4 *m* NaCl

Actual Values for Electrolyte Solutions

It is important to remember that the values just calculated are only *expected* values. As stated earlier, a 0.1 *m* solution of sodium chloride lowers the freezing point *nearly* twice as much as a 0.1 *m* solution of sucrose. The actual values of the colligative properties for all strong electrolytes are *almost* what would be expected based on the number of particles they produce in solution. Some specific examples are given in Table 14-3. The freezing-point depression of a compound that produces two ions per formula unit is almost twice that of a nonelectrolytic solution. The freezing-point depression of a compound that produces three ions per formula unit is almost three times that of a nonelectrolytic solution.

TABLE 14-3 Molal Freezing-Point Depressions for Aqueous Solutions of Ionic Solutes

Solute	Concentration (*m*)	Δt_f observed (°C)	Δt_f nonelectrolyte solution (°C)	$\frac{\Delta t_f \text{ observed}}{\Delta t_f \text{ nonelectrolyte solution}}$
KCl	0.1	−0.345	−0.186	1.85
	0.01	−0.0361	−0.0186	1.94
	0.001	−0.00366	−0.00186	1.97
$MgSO_4$	0.1	−0.225	−0.186	1.21
	0.01	−0.0285	−0.0186	1.53
	0.001	−0.00338	−0.00186	1.82
$BaCl_2$	0.1	−0.470	−0.186	2.53
	0.01	−0.0503	−0.0186	2.70
	0.001	−0.00530	−0.00186	2.84

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FIGURE 14-10 The salts applied to icy roads are electrolytes. They lower the freezing point of water and melt the ice.

Look at the values given for KCl solutions in Table 14-3. The freezing-point depression of a 0.1 *m* KCl solution is only 1.85 times greater than that of a nonelectrolyte solution. However, as the concentration decreases, the freezing-point depression comes closer to the value that is twice that of a nonelectrolytic solution.

The differences between the expected and calculated values are caused by the attractive forces that exist between dissociated ions in aqueous solution. The attraction between the hydrated ions in the solution is small compared with those in the crystalline solid. However, forces of attraction do interfere with the movements of the aqueous ions. The more concentrated a solution is, the closer together the ions are, and the greater the attraction between ions is. Only in very dilute solutions is the average distance between the ions large enough and the attraction between ions small enough for the solute ions to move about almost completely freely.

Peter Debye and Erich Hückel introduced a theory in 1923 to account for this attraction between ions in dilute aqueous solutions. According to this theory, the attraction between dissociated ions of ionic solids in dilute aqueous solutions is caused by an ionic atmosphere that surrounds each ion. This means that each ion is, on average, surrounded by more ions of opposite charge than of like charge. This clustering effect hinders the movements of solute ions. A cluster of hydrated ions can act as a single unit rather than as individual ions. Thus, the effective total concentration is less than expected, based on the number of ions known to be present.

Ions of higher charge attract other ions very strongly. They therefore cluster more and have lower effective concentrations than ions with smaller charge. For example, ions formed by $MgSO_4$ have charges of 2+ and 2–. Ions formed by KCl have charges of 1+ and 1–. Note in Table 14-3 that $MgSO_4$ in a solution does not depress the freezing point as much as the same concentration of KCl.

SECTION REVIEW

1. What colligative properties are displayed by each of the following situations?
   a. Antifreeze is added to a car's cooling system to prevent freezing when the air temperature is below 0°C.
   b. Ice melts on sidewalks after salt has been spread on them.
2. Two moles of a nonelectrolytic solute are dissolved in 1 kg of an unknown solvent. The solution freezes at 7.8°C *below* its normal freezing point. What is the molal freezing-point constant of the unknown solvent? What is your prediction for the identity of the solvent?
3. If two solutions of equal amounts in a U-tube are separated by a semipermeable membrane, will the level of the more-concentrated solution or the less-concentrated solution rise?
4. a. Calculate the expected freezing-point depression of a 0.2 *m* KNO_3 solution.
   b. Will the value you calculated match the actual freezing-point depression for this solution? Why or why not?

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CHAPTER 14 REVIEW

CHAPTER SUMMARY

14-1

- The separation of ions that occurs when an ionic solid dissolves is called dissociation.
- When two different ionic solutions are mixed, a precipitate may form if ions from the two solutions react to form an insoluble compound.
- A net ionic equation for a reaction in aqueous solution includes only compounds and ions that change chemically in the reaction. Spectator ions are ions that do not take part in such a reaction.
- Formation of ions from solute molecules is called ionization. A molecular compound may ionize in a water solution if the attraction of the polar water molecules is strong enough to break the polar-covalent bonds of the solute molecules.
- An H_3O^+ ion is called a hydronium ion.
- All, or almost all, of a dissolved strong electrolyte exists as ions in an aqueous solution, whereas a relatively small amount of a dissolved weak electrolyte exists as ions in an aqueous solution.

Vocabulary

dissociation (425)
hydronium ion (431)
ionization (431)
net ionic equation (429)
spectator ions (429)
strong electrolyte (432)
weak electrolyte (433)

14-2

- Colligative properties of solutions depend only on the total number of solute particles present. Boiling-point elevation, freezing-point depression, vapor-pressure lowering, and osmotic pressure are all colligative properties.
- The molal boiling-point and freezing-point constants are used to calculate boiling-point elevations and freezing-point depressions of solvents containing nonvolatile solutes.
- Electrolytes have a greater effect on the freezing and boiling points of solvents than do nonelectrolytes.
- Except in very dilute solutions, the values of colligative properties of electrolytic solutions are less than expected because of the attraction between ions in solution.

Vocabulary

boiling-point elevation, Δt_b (440)
colligative properties (436)
freezing-point depression, Δt_f (438)
molal boiling-point constant, K_b (440)
molal freezing-point constant, K_f (438)
nonvolatile substance (436)
osmosis (442)
osmotic pressure (442)
semipermeable membranes (442)

REVIEWING CONCEPTS

1. How many moles of ions are contained in 1 L of a 1 M solution of KCl? of $Mg(NO_3)_2$? (14-1)

2. Use Table 14-1 to predict whether each of the following compounds is considered soluble or insoluble:
a. KCl
b. $NaNO_3$
c. AgCl
d. $BaSO_4$
e. $Ca_3(PO_4)_2$
f. $Pb(ClO_3)_2$
g. $(NH_4)_2S$
h. $PbCl_2$ (in cold water)
i. FeS
j. $Al_2(SO_4)_3$ (14-1)

3. What is a net ionic equation? (14-1)

4. a. What is ionization?
b. Distinguish between ionization and dissociation. (14-1)

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5. a. Define and distinguish between strong electrolytes and weak electrolytes.
b. Give two examples of each type. (14-1)

6. What determines the strength with which a solute acts as an electrolyte? (14-1)

7. Distinguish between the use of the terms *strong* and *weak* and the use of the terms *dilute* and *concentrated* when used to describe electrolyte solutions. (14-1)

8. How does the presence of a nonvolatile solute affect each of the following properties of the solvent into which the solute is dissolved?
a. vapor pressure
b. freezing point
c. boiling point
d. osmotic pressure (14-2)

9. Using Figure 14-6 as a guide, make a sketch of a vapor pressure-versus-temperature curve that shows the comparison of pure water, a solution with x amount of solute, and a solution with $2x$ the amount of solute. What is the relationship between Δt_f for the x curve and Δt_f for the $2x$ curve? (14-2)

10. a. Why does the level of the more-concentrated solution rise when two solutions of different concentrations are separated by a semipermeable membrane?
b. When does the level of the solution stop rising?
c. When the level stops rising, what is the net movement of water molecules across the membrane? (14-2)

11. a. Compare the effects of nonvolatile electrolytes with the effects of nonvolatile nonelectrolytes on the freezing and boiling points of solvents in which they are dissolved.
b. Why are such differences observed? (14-2)

12. Why does the actual freezing-point depression of an electrolytic solution differ from the freezing-point depression calculated on the basis of the concentration of particles? (14-2)

PROBLEMS

Dissociation

13. Write the equation for the dissolution of each of the following ionic compounds in water. (Hint: See Sample Problem 14-1.)
a. KI
b. $NaNO_3$
c. $MgCl_2$
d. Na_2SO_4

14. For the compounds listed in the previous problem, determine the number of moles of each ion produced as well as the total number of moles of ions produced when 1 mol of each compound dissolves in water.

15. Write the equation for the dissolution of each of the following in water, and then indicate the total number of moles of solute ions formed.
a. 0.50 mol strontium nitrate
b. 0.50 mol sodium phosphate

Precipitation Reactions

16. Using Table 14-1, write the balanced chemical equation, write the overall ionic equation, identify the spectator ions and possible precipitates, and write the net ionic equation for each of the following reactions. (Hint: See Sample Problem 14-2.)
a. mercury(II) chloride (aq) + potassium sulfide $(aq) \longrightarrow$
b. sodium carbonate (aq) + calcium chloride $(aq) \longrightarrow$
c. copper(II) chloride (aq) + ammonium phosphate $(aq) \longrightarrow$

17. Identify the spectator ions in the reaction between KCl and $AgNO_3$ in an aqueous solution.

18. Copper(II) chloride and lead(II) nitrate react in aqueous solutions by double replacement. Write the balanced chemical equation, the overall ionic equation, and the net ionic equation for this reaction. If 13.45 g of copper(II) chloride react, what is the maximum amount of precipitate that could be formed?

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Freezing-Point Depression of Nonelectrolytes

19. Determine the freezing-point depression of H_2O in each of the following solutions. (Hint: See Sample Problem 14-3.)
a. 1.50 *m* solution of $C_{12}H_{22}O_{11}$ (sucrose) in H_2O
b. 171 g of $C_{12}H_{22}O_{11}$ in 1.00 kg H_2O
c. 77.0 g of $C_{12}H_{22}O_{11}$ in 400. g H_2O

20. Determine the molality of each solution of an unknown nonelectrolyte in water, given the following freezing-point depressions. (Hint: See Sample Problem 14-4.)
a. −0.930°C
b. –3.72°C
c. –8.37°C

21. A solution contains 20.0 g of $C_6H_{12}O_6$ (glucose) in 250. g of water.
a. What is the freezing-point depression of the solvent?
b. What is the freezing point of the solution?

22. How many grams of antifreeze, $C_2H_4(OH)_2$, would be required per 500. g of water to prevent the water from freezing at a temperature of –20.0°C?

23. Pure benzene, C_6H_6, freezes at 5.45°C. A solution containing 7.24 g of $C_2Cl_4H_2$ in 115 g of benzene (specific gravity = 0.879) freezes at 3.55°C. Based on these data, what is the molal freezing-point constant for benzene?

24. If 1.500 g of a solute having a molar mass of 125.0 g were dissolved in 35.00 g of camphor, what would be the resulting freezing point of the solution?

Boiling-Point Elevation of Nonelectrolytes

25. Determine the boiling-point elevation of H_2O in each of the following solutions. (Hint: See Sample Problem 14-5.)
a. 2.5 *m* solution of $C_6H_{12}O_6$ (glucose) in H_2O
b. 3.20 g $C_6H_{12}O_6$ in 1.00 kg H_2O
c. 20.0 g $C_{12}H_{22}O_{11}$ (sucrose) in 500. g H_2O

26. Determine the molality of each water solution given the following boiling points:
a. 100.25°C
b. 101.53°C
c. 102.805°C

Colligative Properties of Electrolytes

27. Given 1.00 *m* aqueous solutions of each of the following electrolytic substances, what is the expected change in the freezing point of the solvent? (Hint: See Sample Problem 14-6.)
a. KI
b. $CaCl_2$
c. $Ba(NO_3)_2$

28. What is the expected change in the freezing point of water for an aqueous solution that is 0.015 *m* $AlCl_3$?

29. What is the expected freezing point of a solution containing 85.0 g of NaCl dissolved in 450. g of water?

30. Determine the expected boiling point of a solution made by dissolving 25.0 g of barium chloride in 0.150 kg of water.

31. The change in the boiling point of water for an aqueous solution of potassium iodide is 0.65°C. Determine the apparent molal concentration of potassium iodide.

32. The freezing point of an aqueous solution of barium nitrate is –2.65°C. Determine the apparent molal concentration of barium nitrate.

33. Calculate the expected freezing point of a solution containing 1.00 kg of H_2O and 0.250 mol of NaCl.

34. Experimental data for a 1.00 *m* MgI_2 aqueous solution indicate an actual change in the freezing point of water of −4.78°C. Determine the expected change in the freezing point of water. Suggest a possible reason for discrepancies between the experimental and the expected values.

MIXED REVIEW

35. Given 0.01 *m* aqueous solutions of each of the following, arrange the solutions in order of increasing change in the freezing point of the solution.
a. NaI
b. $CaCl_2$
c. K_3PO_4
d. $C_6H_{12}O_6$ (glucose)

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36. What is the molal concentration of an aqueous calcium chloride solution that freezes at –2.43°C?

37. a. Write the balanced formula equation that shows the possible products of a double replacement reaction between calcium nitrate and sodium chloride.
b. Using Table 14-1, determine if there is a precipitate.

38. Write a balanced equation to show what occurs when hydrogen bromide dissolves and reacts with water. Include a hydronium ion in the equation.

39. Write the equation for the dissolution of each of the following in water, and then indicate the total number of moles of solute ions formed.
a. 0.275 mol potassium sulfide
b. 0.15 mol aluminum sulfate

40. Calculate the expected change in the boiling point of water in a solution made up of 131.2 g of silver nitrate, $AgNO_3$, in 2.00 kg of water.

41. Nitrous acid, HNO_2, is a weak electrolyte. Nitric acid, HNO_3, is a strong electrolyte. Write equations to represent the ionization of each in water. Include the hydronium ion, and show the appropriate kind of arrow in each case.

42. Find the boiling point of an aqueous solution containing a nonelectrolyte that freezes at –6.51°C.

43. Write a balanced equation for the dissolution of sodium carbonate, Na_2CO_3, in water. Find the number of moles of each ion produced when 0.20 mol of sodium carbonate dissolves. Then find the total number of moles of ions.

44. Given the reaction below and the information in Table 14-1, write the net ionic equation for the reaction.

potassium phosphate (*aq*) + lead (II) nitrate (*aq*)

45. Find the expected freezing point of a water solution that contains 268 g of aluminum nitrate, $Al(NO_3)_3$, in 8.50 kg of water.

CRITICAL THINKING

46. Applying Models
a. You are conducting a freezing-point determination in the laboratory using an aqueous solution of KNO_3. The observed freezing point of the solution is –1.15°C. Using a pure water sample, you recorded the freezing point of the pure solvent on the same thermometer as 0.25°C. Determine the molal concentration of KNO_3. Assume that there are no forces of attraction between ions.
b. You are not satisfied with the result in part (a) because you suspect that you should not ignore the effect of ion interaction. You take a 10.00 mL sample of the solution. After carefully evaporating the water from the solution, you obtain a mass of 0.415 g KNO_3. Determine the actual molal concentration of KNO_3 and the percentage difference between the predicted concentration and the actual concentration of KNO_3. Assume that the solution's density is 1.00 g/mL.

47. Analyzing Information The observed freezing-point depression for electrolyte solutions is sometimes less than the calculated value. Why does this occur? Is the difference greater for concentrated solutions or dilute solutions?

48. Analyzing Information The osmotic pressure of a dilute solution can be calculated as follows.

$\pi = MRT$
π = osmotic pressure
M = concentration in moles per liter
R = ideal gas constant
T = absolute temperature of the solution

How does the osmotic-pressure equation compare with the ideal gas law?

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HANDBOOK SEARCH

49. Common reactions for Group 13 elements are found in the *Elements Handbook*. Review this material and answer the following.
   a. Write net ionic equations for each of the example reactions shown on page 751.
   b. Which reactions did not change when written in net ionic form? Why?

50. Common reactions for Group 14 elements are found in the *Elements Handbook*. Review this material and answer the following.
   a. Write net ionic equations for each of the example reactions shown on page 755.
   b. Which reactions did not change when written in net ionic form? Why?

RESEARCH & WRITING

51. Find out how much salt a large northern city, such as New York City or Chicago, uses on its streets in a typical winter. What environmental problems result from this use of salt? What substitutes for salt are being used to melt ice and snow?

52. Research the role of electrolytes and electrolytic solutions in your body. Find out how electrolytes work in the functioning of nerves and muscles. What are some of the health problems that can arise from an imbalance of electrolytes in body fluids?

ALTERNATIVE ASSESSMENT

53. Performance Determine the freezing point of four different mixtures of water and ethylene glycol (use commercial antifreeze). What mixture shows the lowest freezing point?

54. Performance Find the optimum mixture of salt and ice for reducing the temperature of the chilling bath for an ice-cream freezer. Use your data to write a set of instructions on how to prepare the chilling bath for making ice cream.

55. Performance Using a low-voltage dry cell, assemble a conductivity apparatus. Secure several unknown aqueous solutions of equal molality from your instructor, and use the apparatus to distinguish the electrolytes from the nonelectrolytes. Among those identified as electrolytes, rank their relative strengths as conductors from good to poor.

56. Performance Using equal volumes of the unknown solutions from the preceding activity, explain how you could use the freezing-point depression concept to distinguish the electrolytes from the nonelectrolytes. Explain how you could determine the number of ions contained per molecule among the solutes identified as electrolytes. Design and conduct an experiment to test your theories.

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CHAPTER 15

Acids and Bases

Acids and bases change the color of compounds called indicators.

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Properties of Acids and Bases

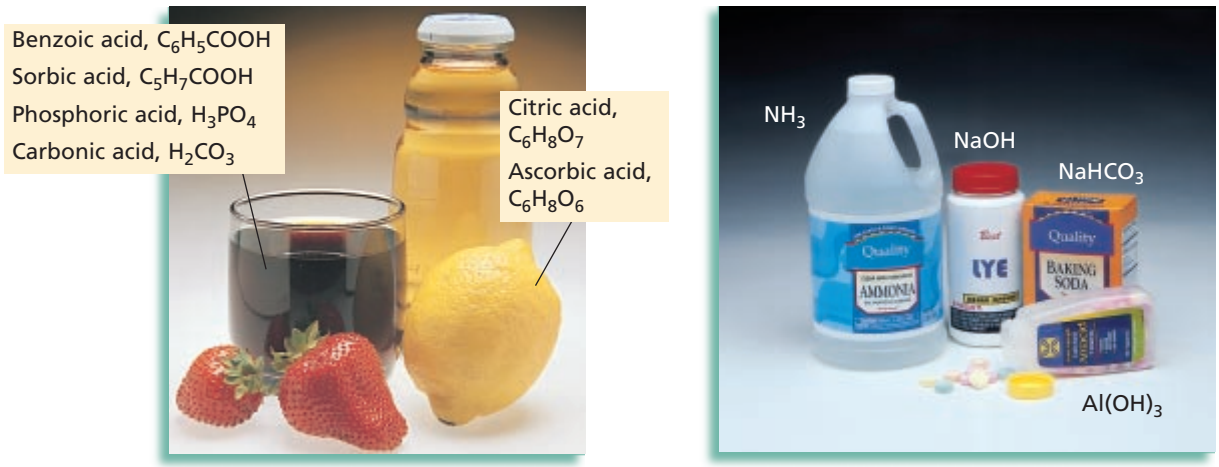
SECTION 15-1

Objectives

- List five general properties of aqueous acids and bases.
- Name common binary acids and oxyacids, given their chemical formulas.
- List five acids commonly used in industry and the laboratory, and give two properties of each.
- Define *acid* and *base* according to Arrhenius's theory of ionization.
- Explain the differences between strong and weak acids and bases.

How many foods can you think of that are sour? Chances are that almost all the foods you thought of, like those in Figure 15-1(a), owe their sour taste to an acid. Sour milk contains *lactic acid.* Vinegar, which can be produced by fermenting juices, contains *acetic acid. Phosphoric acid* gives a tart flavor to many carbonated beverages. Most fruits contain some kind of acid. Lemons, oranges, grapefruits, and other citrus fruits contain *citric acid.* Apples contain *malic acid,* and grape juice contains *tartaric acid*.

Many substances known as bases are commonly found in household products, such as those in Figure 15-1(b). Household ammonia is an ammonia-water solution that is useful for all types of general cleaning. Sodium hydroxide, NaOH, known by the common name *lye,* is present in some commercial drain and oven cleaners. Milk of magnesia is a suspension in water of magnesium hydroxide, $Mg(OH)_2$, which is not very water-soluble. It is used as an antacid to relieve discomfort caused by excess hydrochloric acid in the stomach. Aluminum hydroxide, $Al(OH)_3$, and sodium hydrogen carbonate, $NaHCO_3$, are also bases commonly found in antacids.



(a) (b)

FIGURE 15-1 (a) Fruits and fruit juices contain acids such as citric acid and ascorbic acid. Carbonated beverages contain benzoic acid, phosphoric acid, and carbonic acid. (b) Many household cleaners contain bases such as ammonia and sodium hydroxide.

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FIGURE 15-2 A strip of pH paper dipped into vinegar turns red, showing that vinegar is an acid.

Acids

Acids were first recognized as a distinct class of compounds because of the common properties of their aqueous solutions. These properties are listed below.

1. *Aqueous solutions of acids have a sour taste.* Taste, however, should NEVER be used as a test to evaluate any chemical substance. Many acids, especially in concentrated solutions, are corrosive; that is, they destroy body tissue and clothing. Many are also poisons.
2. *Acids change the color of acid-base indicators.* When pH paper is used as an indicator, the paper turns certain colors in acidic solution. This reaction is demonstrated in Figure 15-2.
3. *Some acids react with active metals to release hydrogen gas, H_2.* Recall that metals can be ordered in terms of an activity series. Metals above hydrogen in the series undergo single-replacement reactions with certain acids. Hydrogen gas is formed as a product, as shown by the reaction of barium with sulfuric acid.

$$Ba(s) + H_2SO_4(aq) \longrightarrow BaSO_4(aq) + H_2(g)$$

4. *Acids react with bases to produce salts and water.* When chemically equivalent amounts of acids and bases react, the three properties just described disappear because the acid is "neutralized." The reaction products are water and an ionic compound called a *salt.*
5. *Some acids conduct electric current.* Acids that form many ions in aqueous solution are electrolytes.

Acid Nomenclature

A **binary acid** *is an acid that contains only two different elements: hydrogen and one of the more electronegative elements.* Many common inorganic acids are binary acids. The hydrogen halides—HF, HCl, HBr, and HI—are all binary acids.

The procedure used to name binary acids is illustrated by the examples given in Table 15-1. In pure form, each acid listed in the table is a gas. Aqueous solutions of these compounds are known by the acid names. From the table you can see that naming binary compounds can be summarized as follows.

TABLE 15-1 *Names of Binary Acids*

Formula	Acid name
HF	hydrofluoric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
H_2S	hydrosulfuric acid

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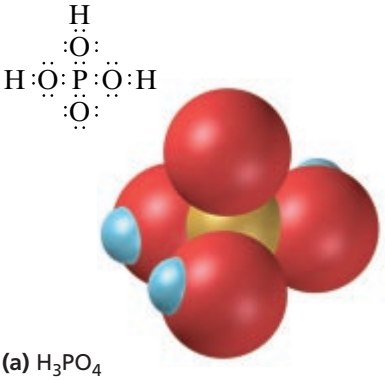
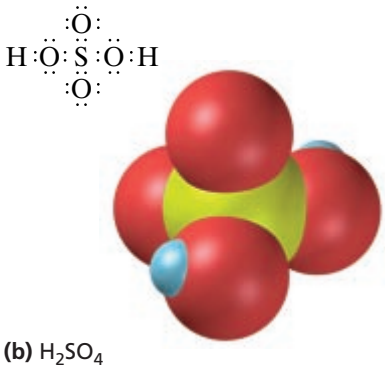


(a) H_3PO_4



(b) H_2SO_4

FIGURE 15-3 Structures of (a) phosphoric acid and (b) sulfuric acid

Binary Acid Nomenclature

1. The name of a binary acid begins with the prefix *hydro-*.
2. The root of the name of the second element follows this prefix.
3. The name then ends with the suffix *-ic*.

An **oxyacid** *is an acid that is a compound of hydrogen, oxygen, and a third element, usually a nonmetal.* Nitric acid, HNO_3, is an oxyacid. The structures of two other oxyacids are shown in Figure 15-3. Oxyacids are one class of ternary acids, which are acids that contain three different elements. Usually, the elements in an oxyacid formula are written as one or more hydrogen atoms followed by a polyatomic anion. The name of an oxyacid is based on this anion. Some common oxyacids and their anions are given in Table 15-2.

TABLE 15-2 *Names of Common Oxyacids and Oxyanions*

Formula	Acid name	Anion
CH_3COOH	acetic acid	CH_3COO^-, acetate
H_2CO_3	carbonic acid	CO_3^{2-}, carbonate
HIO_3	iodic acid	IO_3^-, iodate
$HClO$	hypochlorous acid	ClO^-, hypochlorite
$HClO_2$	chlorous acid	ClO_2^-, chlorite
$HClO_3$	chloric acid	ClO_3^-, chlorate
$HClO_4$	perchloric acid	ClO_4^-, perchlorate
HNO_2	nitrous acid	NO_2^-, nitrite
HNO_3	nitric acid	NO_3^-, nitrate
H_3PO_3	phosphorous acid	PO_3^{3-}, phosphite
H_3PO_4	phosphoric acid	PO_4^{3-}, phosphate
H_2SO_3	sulfurous acid	SO_3^{2-}, sulfite
H_2SO_4	sulfuric acid	SO_4^{2-}, sulfate

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Some Common Industrial Acids

The properties of acids make them important chemicals both in the laboratory and in industry. Sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, and acetic acid are all common industrial acids.

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Sulfuric Acid

Sulfuric acid is the most commonly produced industrial chemical in the world. More than 47 million tons of it are made each year in the United States alone. Sulfuric acid is used in large quantities in petroleum refining and metallurgy as well as in the manufacture of fertilizer. It is also essential to a vast number of industrial processes, including the production of metals, paper, paint, dyes, detergents, and many chemical raw materials. Sulfuric acid is the acid used in automobile batteries.

Because it attracts water, concentrated sulfuric acid is an effective dehydration (water-removing) agent. It can be used to remove water from gases with which it does not react. Sugar and certain other organic compounds are also dehydrated by sulfuric acid. Skin contains organic compounds that are attacked by concentrated sulfuric acid, which can cause serious burns.

Nitric Acid

Pure nitric acid is a volatile, unstable liquid rarely used in industry or laboratories. Dissolving the acid in water provides stability. Nitric acid stains proteins yellow. The feather in Figure 15-4 was stained by nitric acid. The acid has a suffocating odor, stains skin, and can cause serious burns. It is used in making explosives, many of which are nitrogen-containing compounds. It is also used to make rubber, plastics, dyes, and

FIGURE 15-4 Concentrated nitric acid stains a feather yellow.

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pharmaceuticals. Initially, nitric acid solutions are colorless; however, upon standing, they gradually become yellow because of slight decomposition to brown nitrogen dioxide gas.

Phosphoric Acid

Phosphorus, along with nitrogen and potassium, is an essential element for plants and animals. The bulk of phosphoric acid produced each year is used directly for manufacturing fertilizers and animal feed. Dilute phosphoric acid has a pleasant but sour taste and is not toxic. It is used as a flavoring agent in beverages and as a cleaning agent for dairy equipment. Phosphoric acid is also important in the manufacture of detergents and ceramics.

Hydrochloric Acid

The stomach produces HCl to aid in digestion. Industrially, hydrochloric acid is important for "pickling" iron and steel. Pickling is the immersion of metals in acid solutions to remove surface impurities. This acid is also used in industry as a general cleaning agent, in food processing, in the activation of oil wells, in the recovery of magnesium from sea water, and in the production of other chemicals.

A dilute solution of hydrochloric acid, commonly referred to as muriatic acid, may be found in hardware stores. It is used to maintain the correct acidity in swimming pools and for general cleaning of masonry.

Acetic Acid

Concentrated acetic acid is a clear, colorless, pungent-smelling liquid known as glacial acetic acid. This name derives from the fact that pure acetic acid has a freezing point of only 17°C. It can form crystals in a cold room. The fermentation of certain plants produces vinegars containing acetic acid. White vinegar contains 4–8% acetic acid.

Acetic acid is important industrially in synthesizing chemicals used in the manufacture of plastics. It is a raw material in the production of food supplements—for example, lysine, an essential amino acid. Acetic acid is also used as a fungicide.

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Bases

How do bases differ from acids? You can answer this question by comparing the following properties of bases with those of acids.

1. *Aqueous solutions of bases taste bitter.* You may have noticed this fact if you have ever gotten soap, a basic substance, in your mouth. As with acids, taste should NEVER be used to test a substance to see if it is a base. Many bases are caustic; they attack the skin and tissues, causing severe burns.
2. *Bases change the color of acid-base indicators.* As Figure 15-5 shows, an indicator will be a different color in a basic solution than it would be in an acidic solution.

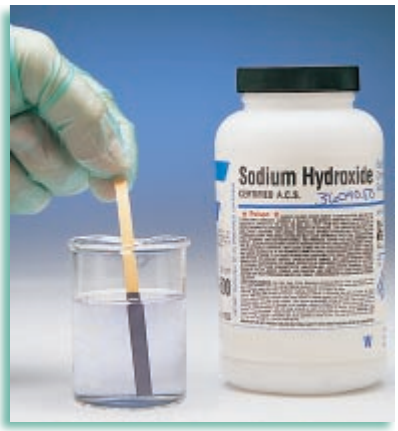

FIGURE 15-5 pH paper turns blue in the presence of this solution of sodium hydroxide.

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Quick LAB

Household Acids and Bases

Wear Safety Goggles and an Apron.

Materials

- dishwashing liquid, dishwasher detergent, laundry detergent, laundry stain remover, fabric softener, and bleach
- fresh red cabbage
- hot plate
- beaker, 500 mL or larger
- beakers, 50 mL
- mayonnaise, baking powder, baking soda, white vinegar, cider vinegar, lemon juice, soft drinks, mineral water, and milk
- spatula
- tap water
- tongs

Question

Which of the household substances are acids, and which are bases?

Procedure

Record all your results in a data table.

1. To make an acid-base indicator, extract juice from red cabbage. First, cut up some red cabbage and place it in a large beaker. Add enough water so that the beaker is half full. Then bring the mixture to a boil. Let it cool, and pour off the cabbage juice. Save the solution.
2. Assemble foods, beverages, and cleaning products to be tested.
3. If the substance being tested is a liquid, pour about 5 mL into a small beaker. If it is a solid, place a small amount into a beaker, and moisten it with about 5 mL of water.
4. Add a drop or two of the red cabbage juice to the solution being tested, and note the color. The solution will turn red if it is acidic and green if it is basic.

Red cabbage can be made into an acid-base indicator.

Discussion

1. Are the cleaning products acids, bases, or neither?
2. What are acid/base characteristics of foods and beverages?
3. Did you find consumer warning labels on basic or acidic products?

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3. *Dilute aqueous solutions of bases feel slippery.* You encounter this property of aqueous bases whenever you wash with soap.
4. *Bases react with acids to produce salts and water.* The properties of an acid disappear with the addition of an equivalent amount of a base. It could also be said that "neutralization" of the base occurs when these two substances react to produce salts and water.
5. *Bases conduct electric current.* Like acids, bases form ions in aqueous solutions and are thus electrolytes.

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Arrhenius Acids and Bases

Svante Arrhenius, a Swedish chemist who lived from 1859 to 1927, understood that aqueous solutions of acids and bases conducted electric current. Arrhenius therefore theorized that acids and bases must produce ions in solution. *An* **Arrhenius acid** *is a chemical compound that increases the concentration of hydrogen ions, H^+, in aqueous solution.* In other words, an acid will ionize in solution, increasing the number of hydrogen ions present. *An* **Arrhenius base** *is a substance that increases the concentration of hydroxide ions, OH^-, in aqueous solution.* Some bases are ionic hydroxides. These bases dissociate in solution to release hydroxide ions into the solution. Other bases are substances that react with water to remove a hydrogen ion, leaving hydroxide ions in the solution.

Aqueous Solutions of Acids

The acids described by Arrhenius are molecular compounds with ionizable hydrogen atoms. Their water solutions are known as *aqueous acids*. All pure aqueous acids are electrolytes.

Acid molecules are sufficiently polar so that one or more hydrogen ions are attracted by water molecules. Negatively charged anions are left behind. As explained in Chapter 14, the hydrogen ion in aqueous solution is best represented as H_3O^+, the hydronium ion. The ionization of an HNO_3 molecule is shown by the following equation. Figure 15-6 shows how the hydrogen atoms combine with water to form a hydronium ion when nitric acid is diluted.

$$HNO_3(l) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Similarly, ionization of a hydrogen chloride molecule in hydrochloric acid can be represented in the following way.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

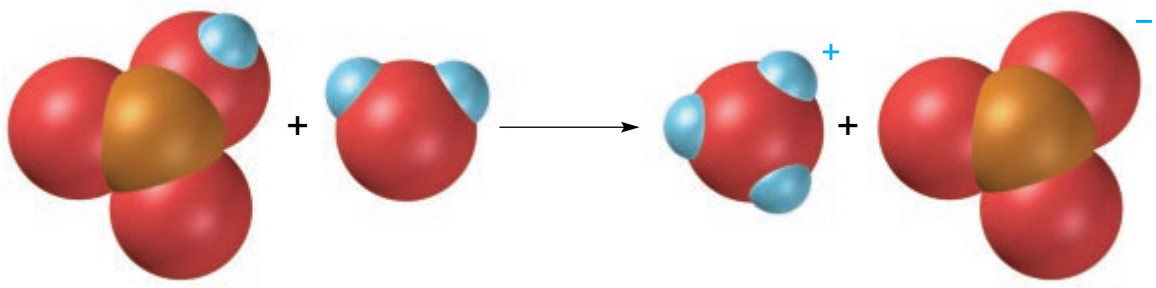

FIGURE 15-6 Arrhenius's observations form the basis of a definition of acids. Arrhenius acids, such as the nitric acid shown here, produce hydronium ions in aqueous solution.

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TABLE 15-3 Common Aqueous Acids

Strong acids		Weak acids	
$H_2SO_4 + H_2O$	$\longrightarrow H_3O^+ + HSO_4^-$	$HSO_4^- + H_2O$	$\rightleftharpoons H_3O^+ + SO_4^{2-}$
$HClO_4 + H_2O$	$\longrightarrow H_3O^+ + ClO_4^-$	$H_3PO_4 + H_2O$	$\rightleftharpoons H_3O^+ + H_2PO_4^-$
$HCl + H_2O$	$\longrightarrow H_3O^+ + Cl^-$	$HF + H_2O$	$\rightleftharpoons H_3O^+ + F^-$
$HNO_3 + H_2O$	$\longrightarrow H_3O^+ + NO_3^-$	$CH_3COOH + H_2O$	$\rightleftharpoons H_3O^+ + CH_3COO^-$
$HBr + H_2O$	$\longrightarrow H_3O^+ + Br^-$	$H_2CO_3 + H_2O$	$\rightleftharpoons H_3O^+ + HCO_3^-$
$HI + H_2O$	$\longrightarrow H_3O^+ + I^-$	$H_2S + H_2O$	$\rightleftharpoons H_3O^+ + HS^-$
		$HCN + H_2O$	$\rightleftharpoons H_3O^+ + CN^-$
		$HCO_3^- + H_2O$	$\rightleftharpoons H_3O^+ + CO_3^{2-}$

Strength of Acids

A **strong acid** *is one that ionizes completely in aqueous solution.* A strong acid is a strong electrolyte. Perchloric acid, $HClO_4$, hydrochloric acid, HCl, and nitric acid, HNO_3, are examples of strong acids. The strength of an acid depends on the polarity of the bond between hydrogen and the element to which it is bonded and the ease with which that bond can be broken. Acid strength increases with increasing polarity and decreasing bond energy.

Acids that are weak electrolytes are known as **weak acids.** The aqueous solution of a weak acid contains hydronium ions, anions, and dissolved acid molecules. Hydrocyanic acid is an example of a weak electrolyte. In aqueous solution, both the ionization of HCN and the reverse reaction occur simultaneously. Although hydronium and cyanide ions are present in solution, the reverse reaction is favored. Most of the solution is composed of hydrogen cyanide and water.

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

Common aqueous acids are listed in Table 15-3. Each strong acid is assumed to ionize completely to give up one hydrogen ion. Notice that the number of hydrogen atoms in the formula does not affect acid strength. Molecules with multiple hydrogen atoms may not readily give up each hydrogen. The fact that phosphoric acid has three hydrogen atoms per molecule does not mean that it is a strong acid. None of these ionize completely in solution, so phosphoric acid is weak.

Organic acids, which contain the acidic carboxyl group —COOH, are generally weak acids. For example, acetic acid, CH_3COOH, ionizes slightly in water to give hydronium ions and acetate ions, CH_3COO^-.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

A molecule of acetic acid contains four hydrogen atoms. However, only one of the hydrogen atoms is ionizable. The hydrogen atom in the

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carboxyl group in acetic acid is the one that is "acidic" and forms the hydronium ion. This acidic hydrogen can be seen in the structural diagram in Figure 15-7.

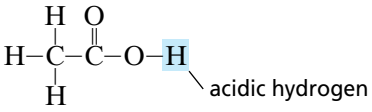

FIGURE 15-7 Acetic acid contains four hydrogen atoms, but only one of them is "acidic" or forms the hydronium ion in solution.

Aqueous Solutions of Bases

Most bases are ionic compounds containing metal cations and the hydroxide anion, OH^-. Because these bases are ionic, they dissociate to some extent when placed in solution. *When a base completely dissociates in water to yield aqueous OH^- ions, the solution is referred to as* **alkaline.** Sodium hydroxide, NaOH, is a common laboratory base. It is water-soluble and dissociates as shown by the equation below.

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

You will remember from Chapter 5 that sodium is one of the alkali metals. This group gets its name from the fact that the hydroxides of Li, Na, K, Rb, and Cs all form alkaline solutions.

Not all bases are ionic compounds. A base commonly used in household cleaners is ammonia, NH_3, which is molecular. Ammonia is a base because it produces hydroxide ions when it reacts with water molecules, as shown in the equation below.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Strength of Bases

As with acids, the strength of a base also depends on the extent to which the base dissociates, or adds hydroxide ions to the solution. For example, potassium hydroxide, KOH, is a strong base because it completely dissociates into its ions in dilute aqueous solutions.

$$KOH(s) \xrightarrow{H_2O} K^+(aq) + OH^-(aq)$$

Strong bases are strong electrolytes, just as strong acids are strong electrolytes. Table 15-4 lists some strong bases.

TABLE 15-4 Common Aqueous Bases

Strong bases	Weak bases
$Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-$	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$Sr(OH)_2 \longrightarrow Sr^{2+} + 2OH^-$	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$
$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$	
$NaOH \longrightarrow Na^+ + OH^-$	
$KOH \longrightarrow K^+ + OH^-$	
$RbOH \longrightarrow Rb^+ + OH^-$	
$CsOH \longrightarrow Cs^+ + OH^-$	

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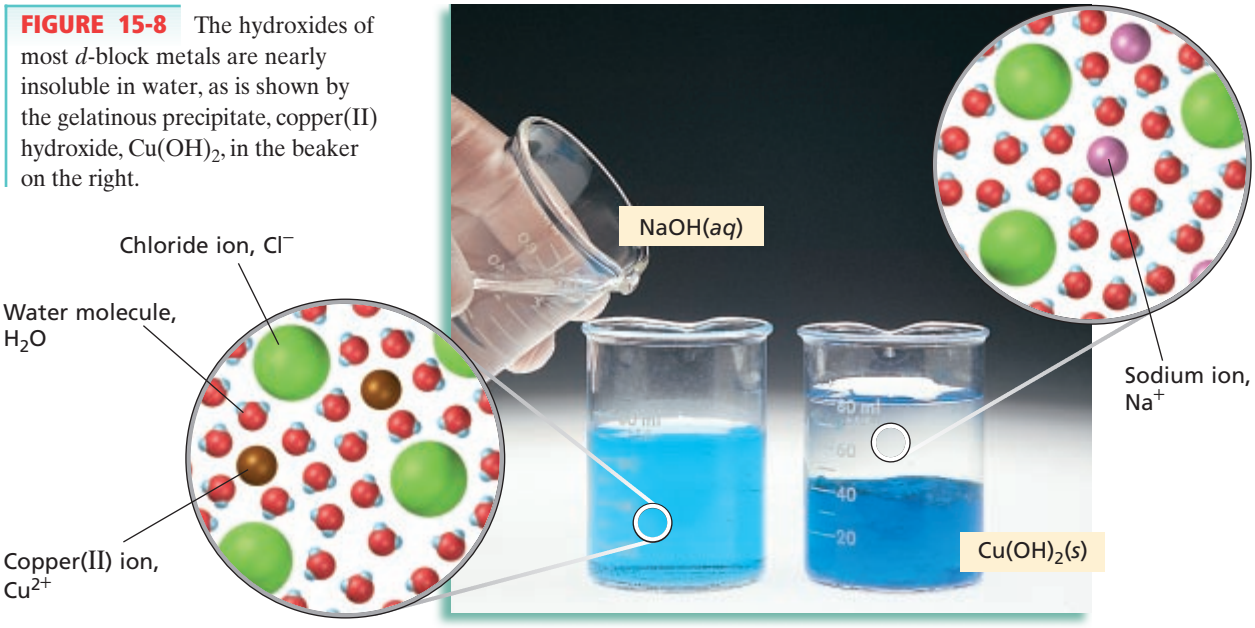

FIGURE 15-8 The hydroxides of most *d*-block metals are nearly insoluble in water, as is shown by the gelatinous precipitate, copper(II) hydroxide, $Cu(OH)_2$, in the beaker on the right.

$$Cu^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s)$$

Bases that are not very soluble do not produce a large number of hydroxide ions when added to water. Some metal hydroxides, such as $Cu(OH)_2$, are not very soluble in water, as seen in Figure 15-8. They cannot produce strongly alkaline solutions. The alkalinity of aqueous solutions depends on the concentration of OH^- ions in solution. It is unrelated to the number of hydroxide ions in the undissolved compound.

Now consider ammonia, which is highly soluble but is a weak electrolyte. The concentration of OH^- ions in an ammonia solution is relatively low. Ammonia is therefore a *weak base*. Many organic compounds that contain nitrogen atoms are also weak bases. For example, aniline, a substance used to make dyes, is a weak base.

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

SECTION REVIEW

1. a. What are five general properties of aqueous acids?
   b. Name some common substances that have one or more of these properties.
2. Name the following acids: a. HBrO b. $HBrO_3$.
3. a. What are five general properties of aqueous bases?
   b. Name some common substances that have one or more of these properties.
4. a. Why are strong acids also strong electrolytes?
   b. Is every strong electrolyte also a strong acid?

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Logic in the Laboratory

From "Acid and Water: A Socratic Dialogue," by David Todd, in *The Journal of Chemical Education.*

Tutor: . . . tell me, how does one set about diluting an acid with water?
Student: The rule is: pour the acid into the water.
Tutor: Why so? . . .
Student: I believe much heat is given off if you do it the wrong way, and the mixture can boil up in your face.
Tutor: Indeed, that is so . . . But is there not heat also developed if you pour the acid into the water?
Student: (thoughtfully) I suppose so. But then I can only assume since there is a rule, that the heat developed is a lot less if you do it that way.
Tutor: Let us reason together. Have you ever heard of Hess's Law?
Student: . . . Doesn't it have something to do with A going to B and the heat change involved?
Tutor: Very good . . . Now suppose I start with 100 g of water in one container at 25°C, and 100 g of concentrated sulfuric acid at 25°C in another container. We can call these two items your A . . . Now let us assume that the two have been mixed—regardless of the mode of mixing—do we not obtain a diluted acid that is 100 g of acid and 100 g of water, and we can call this B?
Student: (cautiously) Well—almost. But . . . concentrated sulfuric acid is 96% by weight H_2SO_4 and 4% water. This means that B is 96 g of pure sulfuric acid and 104 g of water.
Tutor: . . . Oh, excellent! You have had good teachers . . . But the main point is that B has the same composition regardless of the route by which it is obtained. Agreed?
Student: That most assuredly must be so.
Tutor: Now let us return to Hess's Law. It states that the heat change involved in going from A to B is the same regardless of the path taken.
Student: . . . Yes—I remember it now. You mean this law says that the same heat is evolved (or absorbed) if I pour the acid into the water, or vice versa?
Tutor: Yes, indeed.
Student: (now bewildered) You mean that the rule is nonsense, and therefore useless?
Tutor: Oh no, not at all! . . .
Student: . . . Hmm. Then in that case there must be some other factor involved.
Tutor: Indeed there is . . . May I drop a hint? . . . Which is the more dense—concentrated sulfuric acid or water?
Student: The acid . . .
Tutor: Good. Now if I put water on the acid, does it float or sink?
Student: Of course it will stay on the top.
Tutor: Right. And it will begin to mix . . .

Always dilute by pouring acid into water.

Student: I get it—it reacts on the surface, generates a lot of heat, and some of the diluted acid can boil up in my face.
Tutor: Exactly. And if I pour the acid into . . .
Student: (interrupting) Yes, yes—of course. The acid falls down through the water generating the heat in the entire body of the liquid—not just on the surface. So it won't form steam and boil up in my face . . . now I see the reason for the rule.

Reading for Meaning

In your own words, sum up the reason behind the rule for diluting acid with water.

Read Further

Hydrofluoric acid is a fairly weak acid. It does not burn the skin the way sulfuric acid and other strong acids do. Find an explanation of why this acid can greatly damage body tissue when it comes into contact with the skin.

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SECTION 15-2

Acid-Base Theories

Objectives

- Define and recognize *Brønsted-Lowry acids* and *bases.*
- Define a *Lewis acid* and a *Lewis base.*
- Name compounds that are acids under the Lewis definition but are not acids under the Brønsted-Lowry definition.

For most uses, scientists found the Arrhenius definition of acids and bases to be adequate. However, as scientists further investigated acid-base behavior, they found that some substances acted as acids or bases when they were not in a water solution. Because the Arrhenius definition requires that the substances be aqueous, the definitions of acids and bases had to be revised.

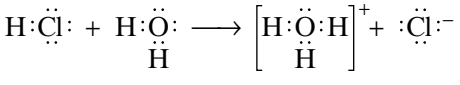
Brønsted-Lowry Acids and Bases

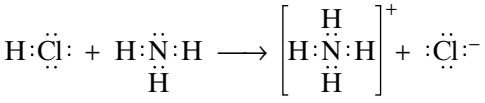
In 1923, the Danish chemist J. N. Brønsted and the English chemist T. M. Lowry independently expanded the Arrhenius acid definition. *A* **Brønsted-Lowry acid** *is a molecule or ion that is a proton donor.* Because H^+ is a proton, all acids as defined by Arrhenius donate protons to water and are Brønsted-Lowry acids as well. Substances other than molecules, such as certain ions, can also donate protons. Such substances are not Arrhenius acids but are included in the category of Brønsted-Lowry acids.

Hydrogen chloride acts as a Brønsted-Lowry acid when it is dissolved in ammonia. It transfers protons to the solvent much as it does in water.

$$HCl + NH_3 \longrightarrow NH_4^+ + Cl^-$$

A proton is transferred from the hydrogen chloride molecule, HCl, to the ammonia molecule, NH_3. The ammonium ion, NH_4^+, is formed. Electron-dot formulas show the similarity of this reaction to the reaction of HCl with water.

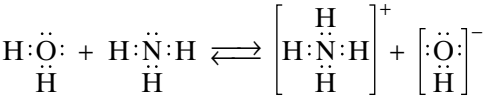




In both reactions, hydrogen chloride is a Brønsted-Lowry acid.

Water can also act as a Brønsted-Lowry acid. Consider, for example, the following reaction, in which the water molecule donates a proton to the ammonia molecule.

$$H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



CHEMISTRY INTERACTIVE TUTOR

Module 8: Strong and Weakly Ionized Species, pH, and Titrations

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FIGURE 15-9 Hydrogen chloride gas escapes from a hydrochloric acid solution and combines with ammonia gas that has escaped from an aqueous ammonia solution. The resulting cloud is solid ammonium chloride.

A **Brønsted-Lowry base** *is a molecule or ion that is a proton acceptor.* In the reaction between hydrochloric acid and ammonia, ammonia accepts a proton from the hydrochloric acid. It is a Brønsted-Lowry base. The Arrhenius hydroxide bases, such as NaOH, are not, strictly speaking, Brønsted-Lowry bases. That is because as compounds they are not proton acceptors. The OH^- ion produced in solution is the Brønsted-Lowry base. It is the species that can accept a proton.

In a **Brønsted-Lowry acid-base reaction,** *protons are transferred from one reactant (the acid) to another (the base).* Figure 15-9 shows the reaction between the Brønsted-Lowry acid HCl and the Brønsted-Lowry base NH_3.

Monoprotic and Polyprotic Acids

An acid that can donate only one proton (hydrogen ion) per molecule is known as a **monoprotic acid.** Perchloric acid, $HClO_4$, hydrochloric acid, HCl, and nitric acid, HNO_3, are all monoprotic. The following equation shows how a molecule of the monoprotic acid HCl donates a proton to a water molecule. HCl is completely ionized; it has no more hydrogen atoms to lose.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

A **polyprotic acid** *is an acid that can donate more than one proton per molecule.* Sulfuric acid, H_2SO_4, and phosphoric acid, H_3PO_4, are examples of polyprotic acids. The ionization of a polyprotic acid occurs in stages. The acid loses its hydrogen atoms one at a time. Sulfuric acid

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ionizes in two stages. In its first ionization, sulfuric acid is a strong acid. It is completely converted to hydrogen sulfate ions, HSO_4^-.

$$H_2SO_4(l) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

The hydrogen sulfate ion is itself a weak acid. It establishes the following equilibrium in solution.

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

All stages of ionization of a polyprotic acid occur in the same solution. Sulfuric acid solutions therefore contain H_3O^+, HSO_4^-, and SO_4^{2-} ions.

Sulfuric acid is the type of polyprotic acid that *can donate two protons per molecule, and it is therefore known as a* **diprotic acid.** Ionizations of a monoprotic acid and a diprotic acid are shown in Figure 15-10.

Phosphoric acid is the type of polyprotic acid known as a **triprotic acid**—*an acid able to donate three protons per molecule.* The equations for these reactions are shown below.

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

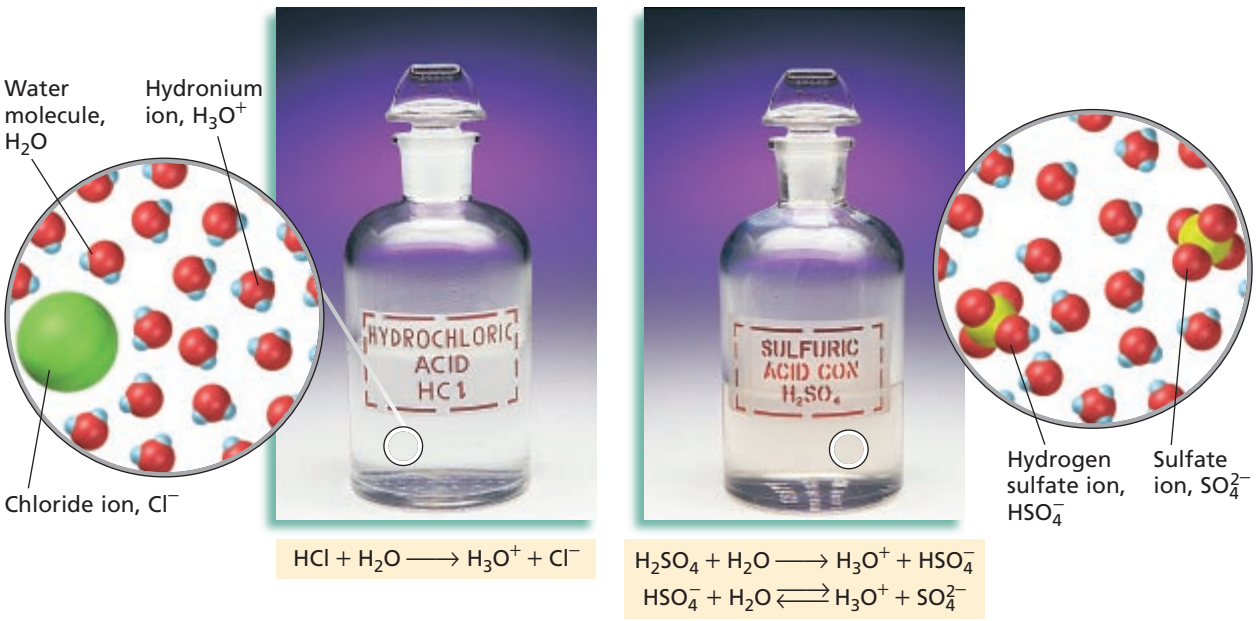
Water molecule, H_2O
Hydronium ion, H_3O^+
Chloride ion, Cl^-
HYDROCHLORIC ACID HCl
SULFURIC ACID CON H_2SO_4
Hydrogen sulfate ion, HSO_4^-
Sulfate ion, SO_4^{2-}
$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$
$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

FIGURE 15-10 Hydrochloric acid, HCl, is a strong monoprotic acid. A dilute HCl solution contains hydronium ions and chloride ions. Sulfuric acid, H_2SO_4, is a strong diprotic acid. A dilute H_2SO_4 solution contains hydrogen sulfate ions from the first ionization, sulfate ions from the second ionization, and hydronium ions from both ionizations.

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A solution of phosphoric acid contains H_3O^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. As with most polyprotic acids, the concentration of ions formed in the first ionization is the greatest. There are lesser concentrations of the respective ions from each succeeding ionization. Phosphoric acid is a weak acid in each step of its ionization.

Lewis Acids and Bases

The Arrhenius and Brønsted-Lowry definitions describe most acids and bases. Both definitions assume that the acid contains or produces hydrogen ions. A third acid classification, based on bonding and structure, includes, as acids, substances that do not contain hydrogen at all. This definition of acids was introduced in 1923 by G. N. Lewis, the American chemist whose name was given to electron-dot structures. Lewis's definition emphasizes the role of electron pairs in acid-base reactions. *A* **Lewis acid** *is an atom, ion, or molecule that accepts an electron pair to form a covalent bond.*

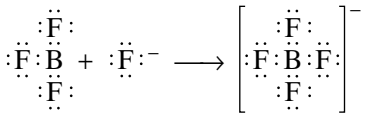
The Lewis definition is the broadest of the three acid definitions you have read about so far. It applies to any species that can accept an electron pair to form a covalent bond with another species. A bare proton (hydrogen ion) is a Lewis acid in reactions in which it forms a covalent bond, as shown below.

$$H^+(aq) + :NH_3(aq) \longrightarrow [H{-}NH_3]^+(aq) \text{ or } [NH_4]^+(aq)$$

The formula for a Lewis acid need not include hydrogen. Even a silver ion can be a Lewis acid, accepting electron pairs from ammonia to form covalent bonds.

$$Ag^+(aq) + 2{:}NH_3(aq) \longrightarrow [H_3N{-}Ag{-}NH_3]^+(aq) \text{ or } [Ag(NH_3)_2]^+$$

Any compound in which the central atom has three valence electrons and forms three covalent bonds can react as a Lewis acid. It does so by accepting a pair of electrons to form a fourth covalent bond, completing an electron octet. Boron trifluoride, for example, is an excellent Lewis acid. It forms a fourth covalent bond with many molecules and ions. Its reaction with a fluoride ion is shown below.



$$BF_3(aq) + F^-(aq) \longrightarrow BF_4^-(aq)$$

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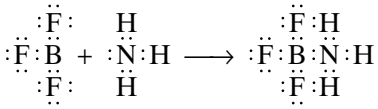
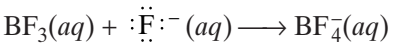
TABLE 15-5 Acid-Base Systems

Type	Acid	Base
Arrhenius	H^+ or H_3O^+ producer	OH^- producer
Brønsted-Lowry	proton (H^+) donor	proton (H^+) acceptor
Lewis	electron-pair acceptor	electron-pair donor

The Lewis definition of acids can apply to species in any phase. For example, boron trifluoride is a Lewis acid in the gas-phase combination with ammonia.



A **Lewis base** *is an atom, ion, or molecule that donates an electron pair to form a covalent bond.* An anion is a Lewis base in a reaction in which it forms a covalent bond by donating an electron pair. In the example of boron trifluoride reacting with the fluoride anion, F^- donates an electron pair to boron trifluoride. F^- acts as a Lewis base.

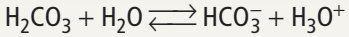


A **Lewis acid-base reaction** *is the formation of one or more covalent bonds between an electron-pair donor and an electron-pair acceptor.*

Note that although the three acid-base definitions differ, many compounds may be categorized as acids or bases according to all three descriptions. For example, ammonia is an Arrhenius base because OH^- ions are created when ammonia is in solution, it is a Brønsted-Lowry base because it accepts a proton in an acid-base reaction, and it is a Lewis base in all reactions in which it donates its lone pair to form a covalent bond. A comparison of the three acid-base definitions is given in Table 15-5.

SECTION REVIEW

1. Label each reactant and each product in the reaction below as a proton donor or a proton acceptor and as acidic or basic.



2. Consider the following three reactions. Identify the Arrhenius bases, Brønsted-Lowry bases, and Lewis bases in these reactions. Explain your answers.

a. $NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$

b. $HF(aq) + H_2O(l) \longrightarrow F^-(aq) + H_3O^+(aq)$

c. $H^+(aq) + NH_3(aq) \longrightarrow NH_4^+(aq)$

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SECTION 15-3

Acid-Base Reactions

Objectives

- Describe a conjugate acid, a conjugate base, and an amphoteric compound.
- Explain the process of neutralization.
- Explain how acid rain damages marble structures.

In the previous section, you learned about three acid-base theories: Arrhenius, Brønsted-Lowry, and Lewis. The Brønsted-Lowry theory is especially useful for describing acid-base reactions that take place in aqueous solutions. This section will use the Brønsted-Lowry description to explore reactions between acids and bases.

Conjugate Acids and Bases

The Brønsted-Lowry definitions of acids and bases provide a basis for studying proton-transfer reactions. Suppose that a Brønsted-Lowry acid gives up a proton; the remaining ion or molecule can re-accept that proton and can act as a base. Such a base is known as a conjugate base. Thus, *the species that remains after a Brønsted-Lowry acid has given up a proton is the* **conjugate base** *of that acid.* For example, the fluoride ion is the conjugate base of hydrogen fluoride.

$$\underset{\text{acid}}{HF(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conjugate base}}{F^-(aq)} + H_3O^+(aq)$$

In this reaction, the water molecule is a Brønsted-Lowry base. It accepts a proton to form H_3O^+, which is an acid. The hydronium ion is the conjugate acid of water. *The species that is formed when a Brønsted-Lowry base gains a proton is the* **conjugate acid** *of that base.*

$$HF(aq) + \underset{\text{base}}{H_2O(l)} \rightleftharpoons F^-(aq) + \underset{\text{conjugate acid}}{H_3O^+(aq)}$$

In general, Brønsted-Lowry acid-base reactions are equilibrium systems meaning that both the forward and reverse reactions occur. They involve two acid-base pairs, known as conjugate acid-base pairs.

$$\underset{\text{acid}_1}{HF(aq)} + \underset{\text{base}_2}{H_2O(l)} \rightleftharpoons \underset{\text{base}_1}{F^-(aq)} + \underset{\text{acid}_2}{H_3O^+(aq)}$$

The subscripts designate the two conjugate acid-base pairs: (1) HF and F^- and (2) H_3O^+ and H_2O. In every conjugate acid-base pair, the acid has one more proton than its conjugate base.

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Strength of Conjugate Acids and Bases

The extent of the reaction between a Brønsted-Lowry acid and base depends on the relative strengths of the acids and bases involved. Consider the following example. Hydrochloric is a strong acid. It gives up protons readily. It follows that the Cl^- ion has little tendency to attract and retain a proton. Consequently, the Cl^- ion is an extremely weak base.

$$\underset{\text{strong acid}}{HCl(g)} + \underset{\text{base}}{H_2O(l)} \longrightarrow \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{weak base}}{Cl^-(aq)}$$

This observation leads to an important conclusion: *the stronger an acid is, the weaker its conjugate base; the stronger a base is, the weaker its conjugate acid.*

This concept allows strengths of different acids and bases to be compared to predict the outcome of a reaction. As an example, consider the reaction of perchloric acid, $HClO_4$, and water.

$$\underset{\text{stronger acid}}{HClO_4(aq)} + \underset{\text{stronger base}}{H_2O(l)} \longrightarrow \underset{\text{weaker acid}}{H_3O^+(aq)} + \underset{\text{weaker base}}{ClO_4^-(aq)}$$

The hydronium ion is too weak an acid to compete successfully with perchloric acid in donating a proton; $HClO_4$ is the stronger acid. In this reaction, the perchlorate ion, ClO_4^-, and H_2O are both bases. Because $HClO_4$ is a very strong acid, ClO_4^- is an extremely weak base. Therefore, H_2O competes more strongly than ClO_4^- to acquire a proton. The reaction proceeds such that the stronger acid reacts with the stronger base to produce the weaker acid and base.

Now consider a comparable reaction between water and acetic acid.

$$\underset{\text{weaker acid}}{CH_3COOH(aq)} + \underset{\text{weaker base}}{H_2O(l)} \longleftarrow \underset{\text{stronger acid}}{H_3O^+(aq)} + \underset{\text{stronger base}}{CH_3COO^-(aq)}$$

The H_3O^+ ion concentration in this solution is much lower than it was in the $HClO_4$ solution because acetic acid is a weak acid. The CH_3COOH molecule does not compete successfully with the H_3O^+ ion in donating protons to a base. The acetate ion, CH_3COO^-, is a stronger base than H_2O. Therefore, the H_2O molecule does not compete successfully with the CH_3COO^- ion in accepting a proton. The H_3O^+ ion is the stronger acid, and the CH_3COO^- ion is the stronger base. Thus, the reaction to the left is more favorable.

Note that in the reactions for both perchloric acid and acetic acid, the favored direction is toward the weaker acid and the weaker base. This observation leads to a second important general conclusion: *proton-transfer reactions favor the production of the weaker acid and the weaker base.* For a reaction to approach completion, the reactants must be much stronger as an acid and as a base than the products.

By comparing many different acids and bases, a table of relative strengths, such as Table 15-6, can be assembled. Note that a very strong acid, such as $HClO_4$, has a very weak conjugate base, ClO_4^-. The strongest base listed in the table, the hydride ion, H^-, has the weakest

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TABLE 15-6 *Relative Strengths of Acids and Bases*

	Conjugate acid	Formula	Conjugate base	Formula	
Strong acids	chloric acid	$HClO_3$	chlorate ion	ClO_3^-	Very weak bases
	hydrobromic acid	HBr	bromide ion	Br^-	
	hydrochloric acid	HCl	chloride ion	Cl^-	
	hydriodic acid	HI	iodide ion	I^-	
	nitric acid	HNO_3	nitrate ion	NO_3^-	
	perchloric acid	$HClO_4$	perchlorate ion	ClO_4^-	
	sulfuric acid	H_2SO_4	hydrogen sulfate ion	HSO_4^-	
	hydronium ion	H_3O^+	water	H_2O	
	chlorous acid	$HClO_2$	chlorite ion	ClO_2^-	
	hydrogen sulfate ion	HSO_4^-	sulfate ion	SO_4^{2-}	
	phosphoric acid	H_3PO_4	dihydrogen phosphate ion	$H_2PO_4^-$	
	hydrofluoric acid	HF	fluoride ion	F^-	
Increasing acid strength	acetic acid	CH_3COOH	acetate ion	CH_3COO^-	Increasing base strength
	carbonic acid	H_2CO_3	hydrogen carbonate ion	HCO_3^-	
	hydrosulfuric acid	H_2S	hydrosulfide ion	HS^-	
	dihydrogen phosphate ion	$H_2PO_4^-$	hydrogen phosphate ion	HPO_4^{2-}	
	hypochlorous acid	HClO	hypochlorite ion	ClO^-	
	ammonium ion	NH_4^+	ammonia	NH_3	
	hydrogen carbonate ion	HCO_3^-	carbonate ion	CO_3^{2-}	
	hydrogen phosphate ion	HPO_4^{2-}	phosphate ion	PO_4^{3-}	
	water	H_2O	hydroxide ion	OH^-	
	ammonia	NH_3	amide ion	NH_2^-	
	hydrogen	H_2	hydride ion	H^-	

conjugate acid, H_2. A violent proton-transfer reaction could result from bringing together a very strong acid and a very strong base in certain proportions because the reaction has almost no tendency to go in the reverse direction. Such a reaction would give off a great deal of heat and would be dangerous. In fact, even the reaction between hydride ions and water—a much weaker acid than perchloric acid—is quite vigorous. The reaction is illustrated in Figure 15-11.

Amphoteric Compounds

You have probably noticed that water can be either an acid or a base. *Any species that can react as either an acid or a base is described as* **amphoteric.** For example, consider the first ionization of sulfuric acid, in which water acts as a base.

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FIGURE 15-11 Because H^- is an extremely strong base, calcium hydride, CaH_2, reacts vigorously with water to produce hydrogen gas. The hydride ion accepts a proton from water, which acts as an acid in this reaction.

$$H^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + H_2(g)$$

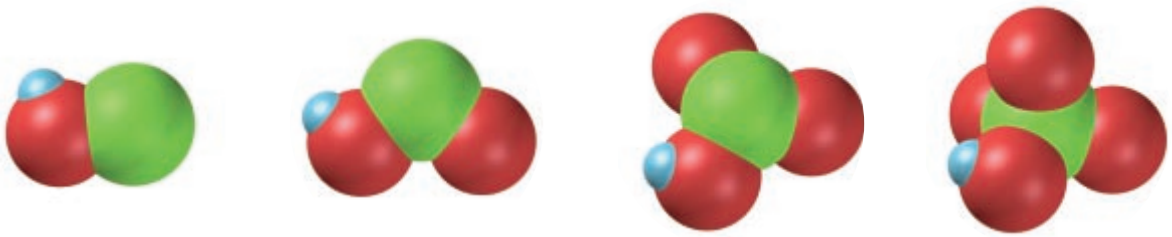
$$\underset{\text{acid}}{H_2SO_4(aq)} + \underset{\text{base}}{H_2O(l)} \longrightarrow \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{HSO_4^-(aq)}$$

However, water acts as an acid in the following reaction.

$$\underset{\text{base}}{NH_3(g)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

Thus, water can act as either an acid or a base and is amphoteric. Such a substance acts as either an acid or a base, depending on the strength of the acid or base with which they are reacting. For example, if water reacts with a compound that is a stronger acid than itself, water acts as a base. If water reacts with a weaker acid, water acts as an acid.

FIGURE 15-12 Each oxyacid of chlorine contains one chlorine atom and one hydrogen atom. They differ in the number of oxygen atoms they contain. The effect of the changing O–H bond polarity can be seen in the increasing acid strength from hypochlorous acid to perchloric acid.



Hypochlorous acid | Chlorous acid | Chloric acid | Perchloric acid

Acidity increases

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–OH in a Molecule

Molecular compounds containing −OH groups can be acidic or amphoteric. The covalently bonded −OH group in an acid is referred to as a *hydroxyl group*. For the compound to be acidic, a water molecule must be able to attract a hydrogen atom from a hydroxyl group. This occurs more easily when the O−H bond is very polar. Any feature of a molecule that increases the polarity of the O−H bond increases the acidity of a molecular compound. The small, more-electronegative atoms of nonmetals at the upper right in the periodic table form compounds with acidic hydroxyl groups. All oxyacids are molecular electrolytes that contain one or more of these O−H bonds. Such compounds include chloric and perchloric acids.

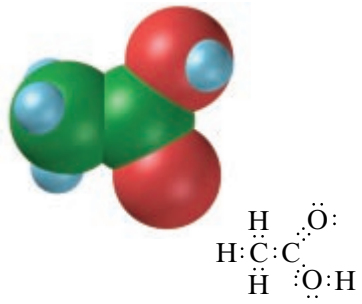
Figure 15-12 shows the electron-dot formulas of the four oxyacids of chlorine. Notice that all of the oxygen atoms are bonded to the chlorine atom. Each hydrogen atom is bonded to an oxygen atom. Aqueous solutions of these molecules are acids because the O−H bonds are broken as the hydrogen is attracted away by water molecules.

The behavior of a compound is affected by the number of oxygen atoms bonded to the atom connected to the – OH group. The larger the number of such oxygen atoms is, the more acidic the compound is likely to be. The electronegative oxygen atoms draw electron density away from the O–H bond and make it more polar. For example, chromium forms three different compounds containing – OH groups, as shown below.

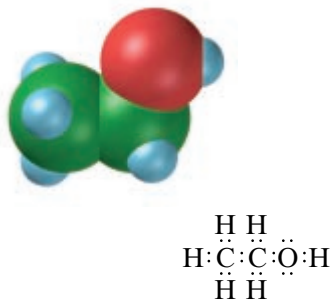
basic	*amphoteric*	*acidic*
$Cr(OH)_2$	$Cr(OH)_3$	H_2CrO_4
chromium(II) hydroxide	chromium(III) hydroxide	chromic acid

Notice that as the number of oxygen atoms increases, so does the acidity of the compound.

Consider also the compounds shown in Figure 15-13. In acetic acid, but not in ethanol, a second oxygen atom is bonded to the carbon atom connected to the –OH group. That explains why acetic acid is acidic but ethanol is not, even though the same elements form each compound.



(a) CH_3COOH
Acetic acid



(b) C_2H_5OH
Ethanol

FIGURE 15-13 (a) Acetic acid is acidic. The second oxygen atom on the carbon draws electron density away from the –OH group, making the O–H bond more polar. (b) Ethanol is essentially neutral. It has no second oxygen atom, so ethanol is less polar than acetic acid, and is a much weaker acid.

Neutralization Reactions

There are many common examples of acidic compounds reacting with basic compounds, each neutralizing the other. Sodium bicarbonate, $NaHCO_3$, and tartaric acid, $C_4H_6O_6$, are two components in baking powder. When allowed to react in solution, the two compounds produce carbon dioxide. The escaping carbon dioxide causes foods, such as biscuits, to rise. An antacid soothes an overly acidic stomach by neutralizing the stomach acid.

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Strong Acid-Strong Base Neutralization

An acid-base reaction occurs in aqueous solution between hydrochloric acid, a strong acid that completely dissociates to produce H_3O^+, and sodium hydroxide, a strong base that completely dissociates to produce OH^-. The formula equation for this reaction is written as follows.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

In an aqueous solution containing 1 mol of sodium hydroxide, NaOH dissociates as represented by the following equation.

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

A solution containing 1 mol of hydrochloric acid ionizes as represented by the following equation.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

If the two solutions are mixed, as in Figure 15-14, a reaction occurs between the aqueous ions. Notice that sodium chloride, NaCl, and water are produced. The overall ionic equation is shown below.

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + 2H_2O(l)$$

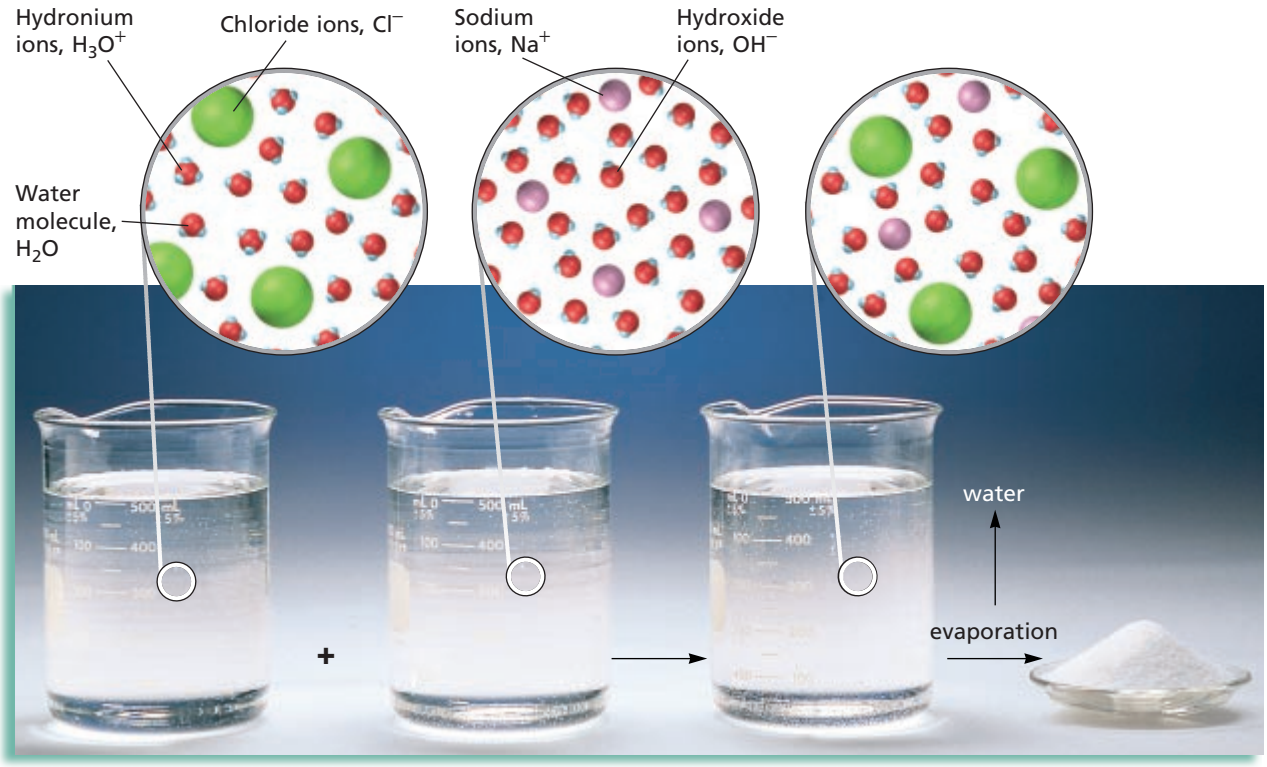

FIGURE 15-14 When aqueous hydrochloric acid, HCl, reacts with aqueous sodium hydroxide, NaOH, the reaction produces aqueous sodium chloride, NaCl. Ions that are present in each solution are represented by the models.

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Because they appear on both sides of the overall ionic equation, Na^+ and Cl^- are spectator ions. The only participants in the reaction are the hydronium ion and the hydroxide ion, as shown in the following net ionic equation.

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

There are equal numbers of H_3O^+ and OH^- ions in this reaction, and they are fully converted to water. In aqueous solutions, **neutralization** *is the reaction of hydronium ions and hydroxide ions to form water molecules.*

Notice that water is not the only product of a neutralization. A salt is also produced. *A* **salt** *is an ionic compound composed of a cation from a base and an anion from an acid.*

Acid Rain

Many industrial processes produce gases such as NO, NO_2, CO_2, SO_2, and SO_3. These compounds can dissolve in atmospheric water to produce acidic solutions that fall to the ground in the form of rain or snow. The following reaction shows how sulfur trioxide, SO_3, dissolves in water to produce sulfuric acid.

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Marble found in many buildings and statues is composed of calcium carbonate, $CaCO_3$. When acid snow or rain falls on these structures, the following reaction takes place.

$$CaCO_3(s) + 2H_3O^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + 3H_2O(l)$$

The products of the reaction of an acid with any carbonate are a salt, water, and carbon dioxide. An example of the effects of acid rain can be seen in Figure 15-15; the marble in this statue has been eroded by the acidic precipitation. Even though the products themselves are harmless, the reaction has serious consequences.

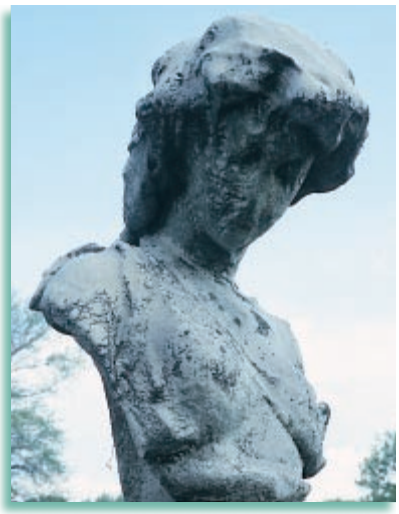

FIGURE 15-15 Acid precipitation causes extensive damage to buildings and other structures.

SECTION REVIEW

1. Complete and balance the equations for the following acid-base reactions:
   a. $H_2CO_3 + Sr(OH)_2 \longrightarrow$
   b. $HClO_4 + NaOH \longrightarrow$
   c. $HBr + Ba(OH)_2 \longrightarrow$
   d. $NaHCO_3 + H_2SO_4 \longrightarrow$
2. Consider the equation for acetic acid plus water.
   $$HC_2H_3O_2 + H_2O \longrightarrow C_2H_3O_2^- + H_3O^+$$
   a. Refer to Table 15-6 to compare the strengths of the two acids in the equation. Do the same for the two bases.
   b. Determine which direction—forward or reverse—is favored in the reaction.
3. Explain how the presence of several oxygen atoms in a compound containing an –OH group can make the compound acidic.

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CHAPTER 15 REVIEW

CHAPTER SUMMARY

15-1

- Acids have a sour taste and react with active metals. They change the colors of acid-base indicators, and react with bases to produce salts and water. Some conduct electricity.
- Bases have a bitter taste, feel slippery to the skin in dilute aqueous solutions, change the colors of acid-base indicators, react with acids to produce salts and water, and conduct electricity.
- An Arrhenius acid contains hydrogen and ionizes in aqueous solution to form hydrogen ions. An Arrhenius base produces hydroxide ions in aqueous solution.
- The strength of an Arrhenius acid or base is determined by the extent to which it ionizes or dissociates in aqueous solutions.

Vocabulary

alkaline (461)
Arrhenius acid (459)
Arrhenius base (459)
binary acid (454)
oxyacid (455)
strong acid (460)
weak acids (460)

15-2

- A Brønsted-Lowry acid is a proton donor. A Brønsted-Lowry base is a proton acceptor.
- A Lewis acid is an electron-pair acceptor. A Lewis base is an electron-pair donor.
- Acids are described as monoprotic, diprotic, or triprotic, depending on whether they can donate one, two, or three protons per molecule, respectively, in aqueous solutions.

Vocabulary

amphoteric (470)
Brønsted-Lowry acid (464)
Brønsted-Lowry acid-base reaction (465)
Brønsted-Lowry base (465)
diprotic acid (466)
Lewis acid (467)
Lewis acid-base reaction (468)
Lewis base (468)
monoprotic acid (465)
polyprotic acid (465)
triprotic acid (466)

15-3

- In every Brønsted-Lowry acid-base reaction, there are two conjugate acid-base pairs.
- A strong acid has a weak conjugate base; a strong base has a weak conjugate acid.
- Proton-transfer reactions favor the production of weaker acids and bases.
- The acidic or basic behavior of a molecule containing −OH groups may depend on the electronegativity of other atoms in the molecule and the number of oxygen atoms bonded to the atom connected to the −OH group.
- A neutralization reaction produces water and an ionic compound called a salt.
- Acid rain neutralizes the calcium carbonate in marble structures, causing them to deteriorate.

Vocabulary

amphoteric (471)
conjugate acid (469)
conjugate base (469)
neutralization (475)
salt (475)

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REVIEWING CONCEPTS

1. Compare and contrast the general properties of acids and bases. (15-1)
2. a. Distinguish between binary acids and oxyacids in terms of their component elements and the systems used in naming them.
   b. Give three examples of each. (15-1)
3. Identify and describe the characteristic properties of five common acids used in industry. Give some examples of the typical uses of each. (15-1)
4. Although HCl(*aq*) exhibits Arrhenius acidic properties, pure HCl gas and HCl dissolved in a nonpolar solvent exhibit no acidic properties in the Arrhenius sense. Explain why. (15-1)
5. a. What distinguishes strong acids from weak acids?
   b. Give two examples of each. (15-1)
6. H_3PO_4, which contains three hydrogen atoms per molecule, is a weak acid, whereas HCl, which contains only one hydrogen atom per molecule, is a strong acid. Explain why. (15-1)
7. a. What determines the strength of an Arrhenius base?
   b. Give one example each of solutions that are strongly and weakly basic. (15-1)
8. Distinguish among a monoprotic, a diprotic, and a triprotic acid. Give an example of each. (15-2)
9. Which of the three acid definitions is the broadest? Explain. (15-2)
10. Define and give an equation to illustrate each of the following:
    a. a conjugate base
    b. a conjugate acid (15-3)
11. a. What is the relationship between the strength of an acid and that of its conjugate base?
    b. What is the relationship between the strength of a base and its conjugate acid? (15-3)
12. a. What trend is there in the favored direction of proton-transfer reactions?
    b. What determines the extent to which a proton-transfer reaction occurs? (15-3)
13. a. What is meant by the term *amphoteric*?
    b. Give an example of a substance or ion with amphoteric characteristics. (15-3)
14. For each reaction listed, identify the proton donor or acid and the proton acceptor or base. Label each conjugate acid-base pair.
    a. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$
    b. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$
    c. $HNO_3 + SO_4^{2-} \longrightarrow HSO_4^- + NO_3^-$ (15-3)
15. Based on the information given in Table 15-6, determine the following relative to HF, H_2S, HNO_3, and CH_3COOH:
    a. strongest acid
    b. weakest acid
    c. strongest conjugate base among the four produced by the acids listed
    d. weakest conjugate base among the four produced (15-3)
16. Explain why the conjugate base of a strong acid is a weak base and the conjugate acid of a strong base is a weak acid. (15-3)

PROBLEMS

Acid Nomenclature

17. Name each of the following binary acids:
    a. HCl
    b. H_2S
18. Name each of the following oxyacids:
    a. HNO_3
    b. H_2SO_3
    c. $HClO_3$
    d. HNO_2
19. Write formulas for each of the following binary acids:
    a. hydrofluoric acid
    b. hydriodic acid
20. Write formulas for each of the following oxyacids:
    a. perbromic acid
    b. chlorous acid
    c. phosphoric acid
    d. hypochlorous acid

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Acid-Base Theory

21. a. Write the balanced equations that describe the two-stage ionization of sulfuric acid in a dilute aqueous solution.
b. How do the degrees of ionization in the two steps compare?

22. Dilute HCl(*aq*) and KOH(*aq*) are mixed in chemically equivalent quantities. Write the following:
a. formula equation for the reaction
b. overall ionic equation
c. net ionic equation

23. Repeat item 22 with $H_3PO_4(aq)$ and NaOH(*aq*).

24. Write the formula equation and net ionic equation for each of the following reactions:
a. $Zn(s) + HCl(aq) \longrightarrow$
b. $Al(s) + H_2SO_4(aq) \longrightarrow$

25. Write the formula equation and net ionic equation for the reaction between Ca(*s*) and HCl(*aq*).

Neutralization Reactions

26. Complete the following neutralization reactions. Balance each reaction, and then write the overall ionic and net ionic equation for each.
a. $HCl(aq) + NaOH(aq) \longrightarrow$
b. $HNO_3(aq) + KOH(aq) \longrightarrow$
c. $Ca(OH)_2(aq) + HNO_3(aq) \longrightarrow$
d. $Mg(OH)_2(aq) + HCl(aq) \longrightarrow$

27. Write the formula equation, the overall ionic equation, and the net ionic equation for the neutralization reaction involving aqueous solutions of H_3PO_4 and $Mg(OH)_2$. Assume that the solutions are sufficiently dilute so that no precipitates form.

28. Write the balanced chemical equation for each of the following reactions between an acid and a carbonate:
a. $BaCO_3(s) + HCl(aq) \longrightarrow$
b. $MgCO_3(s) + HNO_3(aq) \longrightarrow$
c. $Na_2CO_3(s) + H_2SO_4(aq) \longrightarrow$
d. $CaCO_3(s) + H_3PO_4(aq) \longrightarrow$

29. Write the formula equation, the overall ionic equation, and the net ionic equation for a neutralization reaction that would form each of the following salts.
a. $RbClO_4$
b. $BaSO_4$
c. $CaCl_2$
d. K_2SO_4

Stoichiometry

30. Zinc reacts with 100. mL of 6.00 M cold, aqueous sulfuric acid through single replacement.
a. How many grams of zinc sulfate are produced?
b. How many liters of hydrogen gas would be released at STP?

31. A 211 g sample of barium carbonate, $BaCO_3$, is placed in a solution of nitric acid. Assuming that the acid is present in excess, what mass and volume of dry carbon dioxide gas at STP will be produced?

32. A seashell, composed largely of calcium carbonate, is placed in a solution of HCl. As a result, 1500 mL of dry CO_2 gas at STP is produced. The other products are $CaCl_2$ and H_2O.
a. Based on this information, how many grams of $CaCO_3$ are consumed in the reaction?
b. What volume of 2.00 M HCl solution is used in this reaction?

33. *Acid precipitation* is the term generally used to describe rain or snow that is more acidic than normal. One cause of acid precipitation is the formation of sulfuric and nitric acids from various sulfur and nitrogen oxides produced in volcanic eruptions, forest fires, and thunderstorms. In a typical volcanic eruption, for example, 3.50×10^8 kg of SO_2 may be produced. If this amount of SO_2 were converted to H_2SO_4 according to the two-step process given below, how many kilograms of H_2SO_4 would be produced from such an eruption?

$$SO_2 + \tfrac{1}{2}O_2 \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

MIXED REVIEW

34. Suppose that dilute $HNO_3(aq)$ and LiOH(*aq*) are mixed in chemically equivalent quantities. Write the following for the reaction:
a. formula equation
b. overall ionic equation
c. net ionic equation

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35. Write the balanced chemical equation for the reaction between hydrochloric acid and magnesium metal.

36. Write equations for the three-step ionization of phosphoric acid, H_3PO_4. Compare the degree of ionization for the three steps.

37. Name or give the molecular formula for each of the following acids:
a. HF
b. acetic acid
c. phosphorous acid
d. $HClO_4$
e. H_3PO_4
f. hydrobromic acid
g. HClO
h. H_2CO_3
i. sulfuric acid

CRITICAL THINKING

38. Analyzing Conclusions In the eighteenth century, Antoine Lavoisier experimented with oxides such as CO_2 and SO_2. He observed that they formed acidic solutions. His observations led him to infer that for a substance to exhibit acidic behavior, it must contain oxygen. However, today that is known to be incorrect. Provide evidence to refute Lavoisier's conclusion.

HANDBOOK SEARCH

39. Group 16 of the *Elements Handbook* contains a section covering the acid-base chemistry of oxides. Review this material and answer the following:
a. What type of compounds form acidic oxides?
b. What is an acidic anhydride?
c. List three examples of compounds that are classified as acidic anhydrides.
d. What type of compounds form basic oxides? Why are they basic oxides?

40. a. Look at Table 7A in the *Elements Handbook*. What periodic trends do you notice regarding acid-base character of oxides?
b. How is the nature of the product affected by the concentration of NaOH in a reaction with CO_2?

RESEARCH & WRITING

41. Explain how sulfuric acid production serves as a measure of a country's economy. Write a report on your findings.

42. Performance Conduct library research to find out about the buffering of solutions. Include information on why buffering is typically carried out and on the kinds of materials used. Write a brief report on your findings.

43. Obtain some pH paper from your teacher. Determine whether the soil around your house is acidic or basic. Find one type of plant that would grow well in that type of soil and one that would not.

ALTERNATIVE ASSESSMENT

44. Antacids are designed to neutralize excess hydrochloric acid secreted by the stomach during digestion. Carbonates, bicarbonates, and hydroxides are the active ingredients in bringing about the neutralization reactions in the most widely used antacids. Examine the labels of several common antacids, and identify the active ingredients.

45. Performance Design an experiment that compares three brands of antacids in terms of reaction speed and amount of acid neutralized.

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CHAPTER 16

Acid-Base Titration and pH

The pH of solutions is important to the chemistry of life.

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Aqueous Solutions and the Concept of pH

SECTION 16-1

Objectives

- Describe the self-ionization of water.
- Define *pH,* and give the pH of a neutral solution at 25°C.
- Explain and use the pH scale.
- Given $[H_3O^+]$ or $[OH^-]$, find pH.
- Given pH, find $[H_3O^+]$ or $[OH^-]$.

Hydronium Ions and Hydroxide Ions

You have already seen that acids and bases form hydronium ions and hydroxide ions, respectively, in aqueous solutions. However, these ions formed from the solute are not the only such ions present in an aqueous solution. Hydronium ions and hydroxide ions are also provided by the solvent, water.

Self-Ionization of Water

Careful electrical-conductivity experiments have shown that pure water is an extremely weak electrolyte. Water undergoes self-ionization, as shown in the model in Figure 16-1. *In the* **self-ionization of water,** *two water molecules produce a hydronium ion and a hydroxide ion by transfer of a proton.* The following equilibrium takes place.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Conductivity measurements show that concentrations of H_3O^+ and OH^- in pure water are each only 1.0×10^{-7} mol/L of water at 25°C.

There is a standard notation to represent concentration in moles per liter. The formula of the particular ion or molecule is enclosed in brackets, [ ]. For example, the symbol $[H_3O^+]$ means "hydronium ion concentration in moles per liter," or "molar hydronium ion concentration." In water at 25°C, $[H_3O^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M.

The mathematical product of $[H_3O^+]$ and $[OH^-]$ remains constant in water and dilute aqueous solutions at constant temperature. This

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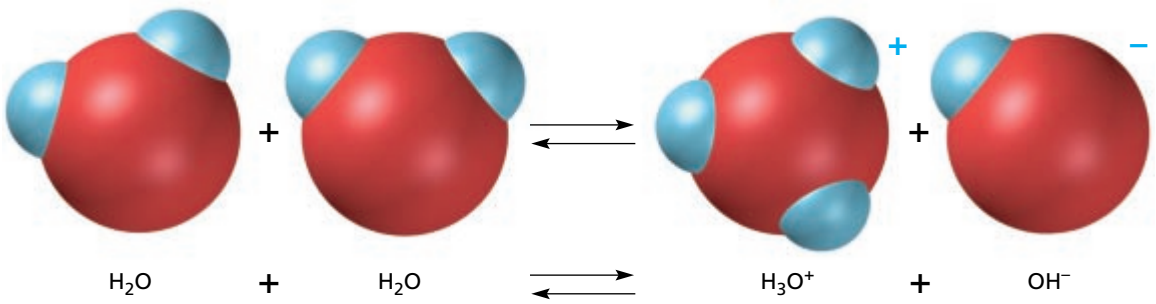

FIGURE 16-1 Water undergoes self-ionization to a slight extent. A proton is transferred from one water molecule to another. A hydronium ion, H_3O^+, and a hydroxide ion, OH^-, are produced.

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TABLE 16-1 K_w at Selected Temperatures

Temperature (°C)	K_w (M^2)
0	1.2×10^{-15}
10	3.0×10^{-15}
25	1.0×10^{-14}
50	5.3×10^{-14}

constant mathematical product is called the *ionization constant of water,* K_w, and is expressed by the following equation.

$$K_w = [H_3O^+][OH^-]$$

For example, in water and dilute aqueous solutions at 25°C, the following relationship is valid.

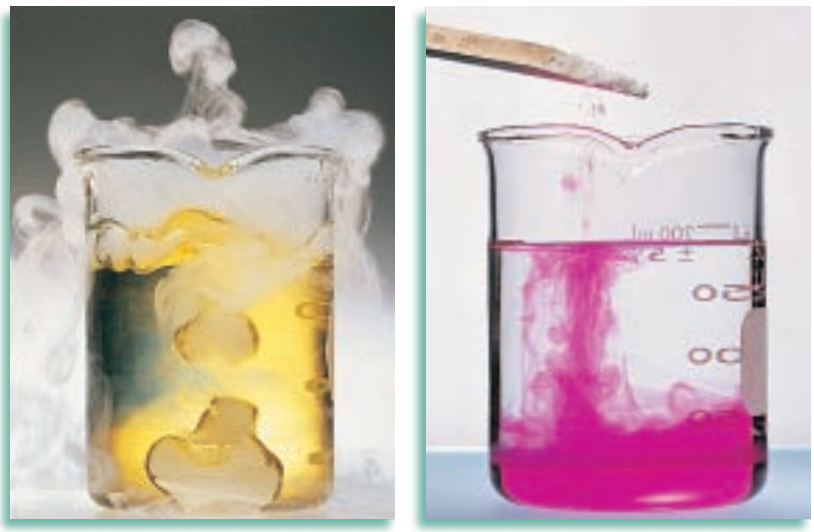
$$K_w = [H_3O^+][OH^-] = (1.0 \times 10^{-7}\ M)(1.0 \times 10^{-7}\ M) = 1.0 \times 10^{-14}\ M^2$$

The ionization of water increases as temperature increases. Therefore, the ion product, K_w, also increases as temperature increases, as shown in Table 16-1. However, at any given temperature K_w is always a constant value. The value $1.0 \times 10^{-14}\ M^2$ is assumed to be constant within the ordinary range of room temperatures. In this chapter, you can assume that these conditions are present unless otherwise stated.

Neutral, Acidic, and Basic Solutions

Because the hydronium ion and hydroxide ion concentrations are the same in pure water, it is *neutral.* Any solution in which $[H_3O^+] = [OH^-]$ is also neutral. Recall from Chapter 15 that acids increase the concentration of H_3O^+ in aqueous solutions, as shown in Figure 16-2(a). Solutions in which the $[H_3O^+]$ is greater than the $[OH^-]$ are *acidic.* Bases increase the concentration of OH^- in aqueous solutions, as shown in Figure 16-2(b). In *basic* solutions, the $[OH^-]$ is greater than the $[H_3O^+]$.

As stated earlier, the $[H_3O^+]$ and the $[OH^-]$ of a neutral solution at 25°C both equal 1.0×10^{-7} M. Therefore, if the $[H_3O^+]$ is increased to greater than 1.0×10^{-7} M, the solution is acidic. A solution containing 1.0×10^{-5} mol H_3O^+ ion/L at 25°C is acidic because 1.0×10^{-5} is greater than 1.0×10^{-7}. If the $[OH^-]$ is increased to greater than 1.0×10^{-7} M, the solution is basic. A solution containing 1.0×10^{-4} mol OH^- ions/L at 25°C is basic because 1.0×10^{-4} is greater than 1.0×10^{-7}.



(a) (b)

FIGURE 16-2 (a) Addition of dry ice, carbon dioxide, to water increases the $[H_3O^+]$, which is shown by the color change of the indicator bromthymol blue to yellow. The white mist is formed by condensation of water droplets because the dry ice is cold. (b) Addition of sodium peroxide to water increases the $[OH^-]$, which is shown by the color change of the indicator phenolphthalein to pink.

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Calculating $[H_3O^+]$ and $[OH^-]$

Recall that strong acids and bases are considered completely ionized or dissociated in weak aqueous solutions. A review of strong acids and bases is given in Table 16-2. Notice that 1 mol of NaOH will yield 1 mol of OH^- in an aqueous solution. Therefore, a 1.0×10^{-2} M NaOH solution has an $[OH^-]$ of 1.0×10^{-2} M, as shown by the following.

$$\underset{1\text{ mol}}{NaOH(s)} \xrightarrow{H_2O} \underset{1\text{ mol}}{Na^+(aq)} + \underset{1\text{ mol}}{OH^-(aq)}$$

$$\frac{1.0 \times 10^{-2}\ \cancel{\text{mol NaOH}}}{\text{L solution}} \times \frac{1\text{ mol } OH^-}{1\ \cancel{\text{mol NaOH}}} = \frac{1.0 \times 10^{-2}\text{ mol } OH^-}{\text{L solution}}$$

$$= 1.0 \times 10^{-2}\text{ M } OH^-$$

Notice that the $[OH^-]$ is greater than 1.0×10^{-7} M. This solution is basic.

Because the K_w of an aqueous solution is a relatively constant 1.0×10^{-14} M^2 at ordinary room temperatures, the concentration of either ion can be determined if the concentration of the other ion is known. The $[H_3O^+]$ of this solution is calculated as follows.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\text{ M}^2$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}\text{ M}^2}{[OH^-]} = \frac{1.0 \times 10^{-14}\text{ M}^2}{1.0 \times 10^{-2}\text{ M}} = 1.0 \times 10^{-12}\text{ M}$$

The $[OH^-]$, 1.0×10^{-2} M, is greater than the $[H_3O^+]$, 1.0×10^{-12} M, as is true for all basic solutions.

Now consider a 1.0×10^{-4} M H_2SO_4 solution. Because H_2SO_4 is a diprotic acid, the $[H_3O^+]$ is 2.0×10^{-4} M, as shown by the following.

$$\underset{1\text{ mol}}{H_2SO_4(l)} + \underset{2\text{ mol}}{2H_2O(l)} \longrightarrow \underset{2\text{ mol}}{2H_3O^+(aq)} + \underset{1\text{ mol}}{SO_4^{2-}(aq)}$$

$$\frac{1.0 \times 10^{-4}\ \cancel{\text{mol } H_2SO_4}}{\text{L solution}} \times \frac{2\text{ mol } H_3O^+}{1\ \cancel{\text{mol } H_2SO_4}} = \frac{2.0 \times 10^{-4}\text{ mol } H_3O^+}{\text{L solution}}$$

$$= 2.0 \times 10^{-4}\text{ M } H_3O^+$$

Notice that the $[H_3O^+]$ is greater than 1.0×10^{-7} M. This solution is acidic. The $[OH^-]$ of this solution is calculated as follows.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\text{ M}^2$$

$$[OH^-] = \frac{1.0 \times 10^{-14}\text{ M}^2}{[H_3O^+]} = \frac{1.0 \times 10^{-14}\text{ M}^2}{2.0 \times 10^{-4}\text{ M}} = 5.0 \times 10^{-10}\text{ M}$$

As is true for all acidic solutions, the $[H_3O^+]$ is greater than the $[OH^-]$.

You may have realized that in order for K_w to remain constant, an increase in either the $[H_3O^+]$ or the $[OH^-]$ in an aqueous solution causes a decrease in the concentration of the other ion. Another example of the calculation of the $[H_3O^+]$ and $[OH^-]$ of an acidic solution is shown in Sample Problem 16-1.

TABLE 16-2 Common Strong Acids and Bases

Strong Acids	Strong Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
$HClO_3$	CsOH
HNO_3	$Ca(OH)_2$
H_2SO_4	$Sr(OH)_2$
	$Ba(OH)_2$

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SAMPLE PROBLEM 16-1

A 1.0×10^{-4} M solution of HNO_3 has been prepared for a laboratory experiment. a. Calculate the $[H_3O^+]$ of this solution. b. Calculate the $[OH^-]$.

SOLUTION

1 ANALYZE

Given: Concentration of the solution = 1.0×10^{-4} M HNO_3
Unknown: a. $[H_3O^+]$ b. $[OH^-]$

2 PLAN

HNO_3 is a strong acid, which means that it is essentially 100% ionized in dilute solutions. One molecule of acid produces one hydronium ion. The concentration of the hydronium ions thus equals the concentration of the acid. Because the ion product, $[H_3O^+]\,[OH^-]$, is a constant, $[OH^-]$ can easily be determined by using the value for $[H_3O^+]$.

a. $\underset{1\text{ mol}}{HNO_3(l)} + \underset{1\text{ mol}}{H_2O(l)} \longrightarrow \underset{1\text{ mol}}{H_3O^+(aq)} + \underset{1\text{ mol}}{NO_3^-(aq)}$ (assuming 100% ionization)

$$\text{molarity of } HNO_3 = \frac{\text{mol } HNO_3}{\text{L solution}}$$

$$\frac{\text{mol } HNO_3}{\text{L solution}} \times \frac{1\text{ mol } H_3O^+}{1\text{ mol } HNO_3} = \frac{\text{mol } H_3O^+}{\text{L solution}} = \text{molarity of } H_3O^+$$

b. $[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}\text{ M}^2$

$$[OH^-] = \frac{1.0 \times 10^{-14}\text{ M}^2}{[H_3O^+]}$$

3 COMPUTE

a. $$\frac{1.0 \times 10^{-4}\ \cancel{\text{mol } HNO_3}}{\text{L solution}} \times \frac{1\text{ mol } H_3O^+}{1\ \cancel{\text{mol } HNO_3}} = \frac{1.0 \times 10^{-4}\text{ mol } H_3O^+}{\text{L solution}} = 1.0 \times 10^{-4}\text{ M } H_3O^+$$

b. $$[OH^-] = \frac{1.0 \times 10^{-14}\text{ M}^2}{[H_3O^+]} = \frac{1.0 \times 10^{-14}\text{ M}^{\cancel{2}}}{1.0 \times 10^{-4}\ \cancel{\text{M}}} = 1.0 \times 10^{-10}\text{ M}$$

4 EVALUATE

Because the $[H_3O^+]$, 1.0×10^{-4}, is greater than 1.0×10^{-7}, the $[OH^-]$ must be less than 1.0×10^{-7}. The answers are correctly expressed to two significant digits.

PRACTICE

1. Determine the hydronium and hydroxide ion concentrations in a solution that is 1×10^{-4} M HCl.
   Answer
   $[H_3O^+] = 1 \times 10^{-4}$ M;
   $[OH^-] = 1 \times 10^{-10}$ M

2. Determine the hydronium and hydroxide ion concentrations in a solution that is 1.0×10^{-3} M HNO_3.
   Answer
   $[H_3O^+] = 1.0 \times 10^{-3}$ M;
   $[OH^-] = 1.0 \times 10^{-11}$ M

3. Determine the hydronium and hydroxide ion concentrations in a solution that is 3.0×10^{-2} M NaOH.
   Answer
   $[H_3O^+] = 3.3 \times 10^{-13}$ M;
   $[OH^-] = 3.0 \times 10^{-2}$ M

4. Determine the hydronium and hydroxide ion concentrations in a solution that is 1.0×10^{-4} M $Ca(OH)_2$.
   Answer
   $[H_3O^+] = 5.0 \times 10^{-11}$ M;
   $[OH^-] = 2.0 \times 10^{-4}$ M

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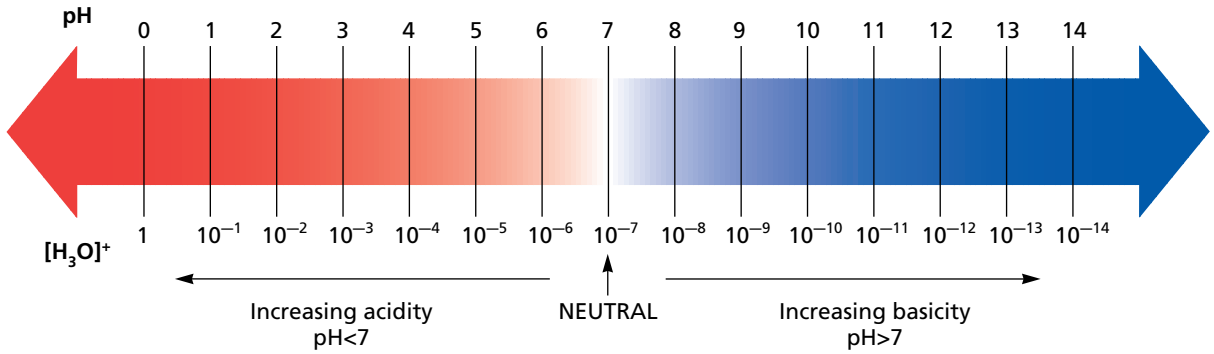

FIGURE 16-3 As the concentration of hydronium ions increases, the solution becomes more acidic and the pH decreases. As the concentration of hydronium ions decreases, the solution becomes more basic and the pH increases.

The pH Scale

Expressing acidity or basicity in terms of the concentration of H_3O^+ or OH^- can be cumbersome because the values tend to be very small. A more convenient quantity, called pH, also indicates the hydronium ion concentration of a solution. The letters *pH* stand for the French words *pouvoir hydrogène,* meaning "hydrogen power." *The* **pH** *of a solution is defined as the negative of the common logarithm of the hydronium ion concentration,* $[H_3O^+]$. The pH is expressed by the following equation.

$$pH = -\log [H_3O^+]$$

The common logarithm of a number is the power to which 10 must be raised to equal the number. A neutral solution at 25°C has a $[H_3O^+]$ of 1×10^{-7} M. The logarithm of 1×10^{-7} is –7.0. The pH is determined as follows.

$$pH = -\log [H_3O^+] = -\log (1 \times 10^{-7}) = -(-7.0) = 7.0$$

The relationship between the pH and $[H_3O^+]$ is shown on the scale in Figure 16-3.

Likewise, the **pOH** *of a solution is defined as the negative of the common logarithm of the hydroxide ion concentration,* $[OH^-]$.

$$pOH = -\log[OH^-]$$

A neutral solution at 25°C has a $[OH^-]$ of 1×10^{-7} M. Therefore, the pOH is 7.0.

Remember that the values of $[H_3O^+]$ and $[OH^-]$ are related by K_w. The negative logarithm of K_w at 25°C, 1×10^{-14}, is 14.0. You may have noticed that the sum of the pH and the pOH of a neutral solution at 25°C is also equal to 14.0. The following relationship is true at 25°C.

$$pH + pOH = 14.0$$

At 25°C the range of pH values of aqueous solutions generally falls between 0 and 14, as shown in Table 16-3.

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TABLE 16-3 *Approximate pH Range of Some Common Materials (at 25°C)*

Material	pH	Material	pH
Gastric juice	1.0–3.0	Bread	5.0–6.0
Lemons	2.2–2.4	Rainwater	5.4–5.8
Vinegar	2.4–3.4	Potatoes	5.6–6.0
Soft drinks	2.0–4.0	Milk	6.3–6.6
Apples	2.9–3.3	Saliva	6.5–7.5
Grapefruit	3.0–3.3	Pure water	7.0
Oranges	3.0–4.0	Blood	7.3–7.5
Cherries	3.2–4.0	Eggs	7.6–8.0
Tomatoes	4.0–4.4	Sea water	8.0–8.5
Bananas	4.5–5.7	Milk of magnesia	10.5

Suppose the $[H_3O^+]$ in a solution is greater than the $[OH^-]$, as is true for acidic solutions. For example, the pH of an acidic solution at 25°C with a $[H_3O^+]$ of 1×10^{-6} M is 6.0.

$$pH = -\log [H_3O^+] = -\log (1 \times 10^{-6}) = -(-6.0) = 6.0$$

The pH of this solution is less than 7. This is the case for all acidic solutions at 25°C. The following calculation shows that the pOH is greater than 7.0, as is true for all acidic solutions at 25°C.

$$pOH = 14.0 - pH = 14.0 - 6.0 = 8.0$$

Similar calculations show that the pH of a basic solution at 25°C is more than 7.0 and the pOH is less than 7.0. These and other relationships are listed in Table 16-4. Remember that as the temperature changes, the exact values will change because the value of K_w changes. However, the relationships between the values will remain the same.

CHEMISTRY INTERACTIVE TUTOR

Module 8: Strong and Weakly Ionized Species, pH, and Titrations

TABLE 16-4 *$[H_3O^+]$, $[OH^-]$, pH, and pOH of Solutions*

Solution	General condition	At 25°C
Neutral	$[H_3O^+] = [OH^-]$ $pH = pOH$	$[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ M $pH = pOH = 7.0$
Acidic	$[H_3O^+] > [OH^-]$ $pH < pOH$	$[H_3O^+] > 1 \times 10^{-7}$ M $[OH^-] < 1 \times 10^{-7}$ M $pH < 7.0$ $pOH > 7.0$
Basic	$[H_3O^+] < [OH^-]$ $pH > pOH$	$[H_3O^+] < 1 \times 10^{-7}$ M $[OH^-] > 1 \times 10^{-7}$ M $pH > 7.0$ $pOH < 7.0$

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Calculations Involving pH

If either the $[H_3O^+]$ or pH of a solution is known, the other can be calculated. Significant figures involving pH must be handled carefully. Because pH represents a logarithm, the number to the *left of the decimal* only locates the decimal point. It is not included when counting significant figures. So there must be as many significant figures to the *right of the decimal* as there are in the number whose logarithm was found. For example, a $[H_3O^+]$ value of 1×10^{-7} has *one* significant figure. Therefore, the pH, or –log, of this value must have one digit to the right of the decimal. Thus, pH = 7.0 has the correct number of significant figures.

Calculating pH from $[H_3O^+]$

You have already seen the simplest pH problems. In these problems, the $[H_3O^+]$ of the solution is an integral power of 10, such as 1 M or 0.01 M. The pH of this type of solution is the exponent of the hydronium ion concentration with the sign changed. For example, the pH of a solution in which $[H_3O^+]$ is 1×10^{-5} M is 5.0.

SAMPLE PROBLEM 16-2

What is the pH of a 1.0×10^{-3} M NaOH solution?

SOLUTION

1 ANALYZE

Given: Identity and concentration of solution = 1.0×10^{-3} M NaOH
Unknown: pH of solution

2 PLAN

concentration of base ⟶ concentration of OH^- ⟶ concentration of H_3O^+ ⟶ pH

NaOH is completely dissociated when it is dissolved in water. A 1.0×10^{-3} M NaOH solution therefore produces a $[OH^-]$ equal to 1.0×10^{-3} M. The ion product of $[H_3O^+]$ and $[OH^-]$ is a constant, 1.0×10^{-14} M^2. By substitution, the $[H_3O^+]$ can be determined. The pH can then be calculated.

3 COMPUTE

$$[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}\ M^2$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}\ M^2}{[OH^-]} = \frac{1.0 \times 10^{-14}\ M^{\cancel{2}}}{1.0 \times 10^{-3}\ \cancel{M}} = 1.0 \times 10^{-11}\ M$$

$$pH = -\log\,[H_3O^+] = -\log\,(1.0 \times 10^{-11}) = 11.00$$

4 EVALUATE

The answer correctly indicates that NaOH forms a solution with pH > 7, which is basic.

PRACTICE

1. Determine the pH of the following solutions:
   a. 1×10^{-3} M HCl
   b. 1×10^{-5} M HNO_3
   c. 1×10^{-4} M NaOH
   d. 1.0×10^{-2} M KOH

Answer
a. pH = 3.0
b. pH = 5.0
c. pH = 10.0
d. pH = 12.00

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Using a Calculator to Calculate pH from $[H_3O^+]$

Some problems involve hydronium ion concentrations that are not equal to integral powers of 10. These problems require a calculator. Most scientific calculators have a "log" key. Consult the instructions for your particular calculator.

An estimate of pH can be used to check your calculations. For example, suppose the $[H_3O^+]$ of a solution is 3.4×10^{-5} M. Because 3.4×10^{-5} lies between 10^{-4} and 10^{-5}, the pH of the solution must be between 4 and 5. Sample Problem 16-3 continues the actual calculation of the pH value for a solution with $[H_3O^+] = 3.4 \times 10^{-5}$ M.

SAMPLE PROBLEM 16-3

What is the pH of a solution if the $[H_3O^+]$ is 3.4×10^{-5} M?

SOLUTION

1 ANALYZE

Given: $[H_3O^+] = 3.4 \times 10^{-5}$ M
Unknown: pH of solution

2 PLAN

$$[H_3O^+] \longrightarrow \text{pH}$$

The only difference between this problem and previous pH problems is that you will determine the logarithm of 3.4×10^{-5} using your calculator. You can convert numbers to logarithms on most calculators by using the "log" key.

3 COMPUTE

$$\begin{aligned} \text{pH} &= -\log [H_3O^+] \\ &= -\log (3.4 \times 10^{-5}) \\ &= 4.47 \end{aligned}$$

On most calculators, this problem is entered in the following steps.

4 EVALUATE

The pH of a 1×10^{-5} M H_3O^+ solution is 5.0. Therefore, it follows that a solution with a greater concentration of hydronium ions would be more acidic and have a pH less than 5.

PRACTICE

1. What is the pH of a solution if the $[H_3O^+]$ is 6.7×10^{-4} M?
   Answer pH = 3.17
2. What is the pH of a solution with a hydronium ion concentration of 2.5×10^{-2} M?
   Answer pH = 1.60
3. Determine the pH of a 2.5×10^{-6} M HNO_3 solution.
   Answer pH = 5.60
4. Determine the pH of a 2.0×10^{-2} M $Sr(OH)_2$ solution.
   Answer pH = 12.60

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Calculating $[H_3O^+]$ and $[OH^-]$ from pH

You have now learned to calculate the pH of a solution, given its $[H_3O^+]$. Suppose that you are given the pH of a solution instead. How can you determine its hydronium ion concentration?

You already know the following equation.

$$pH = -\log [H_3O^+]$$

Remember that the base of common logarithms is 10. Therefore, the antilog of a common logarithm is 10 raised to that number.

$$\log [H_3O^+] = -pH$$
$$[H_3O^+] = \text{antilog}\,(-pH)$$
$$[H_3O^+] = 10^{-pH}$$

The simplest cases are those in which pH values are integers. The exponent of 10 that gives the $[H_3O^+]$ is the negative of the pH. For an aqueous solution that has a pH of 2, for example, the $[H_3O^+]$ is equal to 10^{-2} M. Likewise, when the pH is 0, the $[H_3O^+]$ is 1 M because $10^0 = 1$. Sample Problem 16-4 shows how to convert a pH value that is a positive integer. Sample Problem 16-5 shows how to use a calculator to convert a pH that is not an integral number.

SAMPLE PROBLEM 16-4

Determine the hydronium ion concentration of an aqueous solution that has a pH of 4.0.

SOLUTION

1 ANALYZE

Given: pH = 4.0
Unknown: $[H_3O^+]$

2 PLAN

$$pH \longrightarrow [H_3O^+]$$

This problem requires that you rearrange the pH equation and solve for the $[H_3O^+]$. Because 4.0 has one digit to the right of the decimal, the answer must have one significant figure.

$$pH = -\log [H_3O^+]$$
$$\log [H_3O^+] = -pH$$
$$[H_3O^+] = \text{antilog}\,(-pH)$$
$$[H_3O^+] = 1 \times 10^{-pH}$$

3 COMPUTE

$$[H_3O^+] = 1 \times 10^{-pH}$$
$$[H_3O^+] = 1 \times 10^{-4}\ \text{M}$$

4 EVALUATE

A solution with a pH of 4.0 is acidic. The answer, 1×10^{-4} M, is greater than 1.0×10^{-7} M, which is correct for an acidic solution.

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SAMPLE PROBLEM 16-5

The pH of a solution is measured and determined to be 7.52.
a. What is the hydronium ion concentration? **c. Is the solution acidic or basic?**
b. What is the hydroxide ion concentration?

SOLUTION

1 ANALYZE

Given: pH of the solution = 7.52
Unknown: **a.** $[H_3O^+]$ **b.** $[OH^-]$ **c.** Is the solution acidic or basic?

2 PLAN

$$\text{pH} \longrightarrow [H_3O^+] \longrightarrow [OH^-]$$

This problem is very similar to previous pH problems. You will need to substitute values into the pH = –log $[H_3O^+]$ equation and use a calculator. Once the $[H_3O^+]$ is determined, the ion-product constant $[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$ may be used to calculate $[OH^-]$.

3 COMPUTE

a. $\text{pH} = -\log [H_3O^+]$

$\log [H_3O^+] = -\text{pH}$

$[H_3O^+] = \text{antilog}\,(-\text{pH}) = \text{antilog}\,(-7.52) = 1.0 \times 10^{-7.52} = 3.0 \times 10^{-8}\ \text{M}\ H_3O^+$

On most calculators, this is entered in one of the following two ways.

7 . 5 2 +/– 2nd 10^x *or* 7 . 5 2 +/– INV LOG

b. $[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}\ \text{M}^2$

$$[OH^-] = \frac{1.0 \times 10^{-14}\ \text{M}^2}{[H_3O^+]}$$

$$= \frac{1.0 \times 10^{-14}\ \text{M}^{\cancel{2}}}{3.0 \times 10^{-8}\ \cancel{\text{M}}} = 3.3 \times 10^{-7}\ \text{M}\ OH^-$$

c. A pH of 7.52 is slightly greater than a pH of 7. This means that the solution is slightly basic.

4 EVALUATE

Because the solution is slightly basic, a hydroxide ion concentration slightly larger than 10^{-7} M is predicted. A hydronium ion concentration slightly less than 10^{-7} M is also predicted. The answers agree with these predictions.

PRACTICE

1. The pH of a solution is determined to be 5.0. What is the hydronium ion concentration of this solution?
   Answer $[H_3O^+] = 1 \times 10^{-5}$ M
2. The pH of a solution is determined to be 12.0. What is the hydronium ion concentration of this solution?
   Answer $[H_3O^+] = 1 \times 10^{-12}$ M
3. The pH of an aqueous solution is measured as 1.50. Calculate the $[H_3O^+]$ and the $[OH^-]$.
   Answer $[H_3O^+] = 3.2 \times 10^{-2}$ M; $[OH^-] = 3.2 \times 10^{-13}$ M
4. The pH of an aqueous solution is 3.67. Determine $[H_3O^+]$.
   Answer $[H_3O^+] = 2.1 \times 10^{-4}$ M

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TABLE 16-5 *Relationship of $[H_3O^+]$ to $[OH^-]$ and pH (at 25°C)*

Solution	$[H_3O^+]$	$[OH^-]$	pH
1.0×10^{-2} M KOH	1.0×10^{-12}	1.0×10^{-2}	12.00
1.0×10^{-2} M NH_3	2.4×10^{-11}	4.2×10^{-4}	10.62
Pure H_2O	1.0×10^{-7}	1.0×10^{-7}	7.00
1.0×10^{-3} M HCl	1.0×10^{-3}	1.0×10^{-11}	3.00
1.0×10^{-1} M CH_3COOH	1.3×10^{-3}	7.7×10^{-12}	2.88

pH Calculations and the Strength of Acids and Bases

So far, we have discussed the pH of solutions that contain only strong acids or strong bases. We must also consider weak acids and weak bases. Table 16-5 lists the $[H_3O^+]$, the $[OH^-]$, and the pH for several solutions.

KOH, the solute in the first solution listed, is a soluble ionic compound and a strong base. The molarity of a KOH solution directly indicates the $[OH^-]$, and the $[H_3O^+]$ can be calculated. Once the $[H_3O^+]$ is known, the pH can be calculated as in Sample Problem 16-3. If the pH of this solution is measured experimentally, it will be the same as this calculated value. Methods for experimentally determining the pH of solutions will be presented in Section 16-2. Hydrochloric acid, HCl, is a strong acid, and similar calculations can be made for solutions that contain HCl.

Solutions of weak acids, such as acetic acid, CH_3COOH, present a different problem. The $[H_3O^+]$ cannot be calculated directly from the molar concentration because not all of the acetic acid molecules are ionized. The same problem occurs for weak bases such as ammonia, NH_3. The pH of these solutions must be measured experimentally. The $[H_3O^+]$ and $[OH^-]$ can then be calculated from the measured pH values.

SECTION REVIEW

1. What is the concentration of hydronium and hydroxide ions in pure water at 25°C?
2. Why does the pH scale generally range from 0 to 14 in aqueous solutions?
3. Why does a pH of 7 represent a neutral solution at 25°C?
4. Identify each of the following as being true of acidic or basic solutions at 25°C:
   a. $[H_3O^+] = 1 \times 10^{-3}$ M
   b. $[OH^-] = 1 \times 10^{-4}$ M
   c. pH = 5.0
   d. pH = 8.0
5. A solution contains 4.5×10^{-3} HCl. Determine the following for the solution:
   a. $[H_3O^+]$ b. $[OH^-]$ c. pH
6. A $Ca(OH)_2$ solution has a pH of 8.0. Determine the following for the solution:
   a. $[H_3O^+]$ b. $[OH^-]$ c. $[Ca(OH)_2]$

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Liming Streams

In 1987, Dr. Ken Simmons tested some rainbow trout in the waters of north-central Massachusetts' Whetstone Brook. He placed the trout in cages in the brook so that their behavior and survival could be monitored. Three days later, they were all dead. Acid rain had lowered the pH level of the water to a point at which the trout simply could not survive.

Acid rain begins with the fossil fuels we burn to power our cars and factories. The fumes released by those fuels contain sulfur dioxides and nitrous oxides that combine with the water vapor in the atmosphere and turn it acidic. While normal rainwater has a pH level around 5.7, acid rain's pH can be less than 4.2.

Biologists studied trout to determine the effectiveness of liming Whetstone Brook to raise the pH.

The rain lowers the pH level of the brook and significantly affects most of the organisms living in it. Some fish, like the rainbow trout, simply die. Other species refuse to spawn in acidic waters, as the Whetstone's brown trout did in 1987.

The year that the brown trout refused to spawn, the pH level of Whetstone Brook averaged 5.97. The population of all the trout dropped dangerously low, and in 1989, Dr. Simmons and other researchers instituted an experiment to decrease the acidity of the stream. They created a system to constantly add calcium carbonate, or limestone, in measured amounts to part of the brook. The limestone, ground into a powder, dissolved instantly and acted as a buffer against the acid, raising the pH level of the water.

The experiment lasted three years and managed to raise the average pH level of the stream from 5.97 to 6.54, meeting the scientists' goal. At the same time, the amount of toxic aluminum in the limed area decreased, while it increased in untreated parts of the brook.

The success of the project was most convincingly demonstrated by the stream's residents. The population of brook trout increased, the mortality rate of brown trout decreased, and for the first time in years, fish actually began to move into the stream from its source, the Millers River. In 1991, Dr. Simmons again tested rainbow trout in the waters of the Whetstone. This time, they all survived.

"We clearly don't view it as a solution," says Dr. Simmons. "It's a band-aid approach, but we need data to make intelligent management decisions as to how useful or harmful liming could be. And I think that is the key thing this study has shown. It has provided us with information that we can use."

Describe two possible benefits of adding measured amounts of $CaCO_3$, a base, to an acidified stream.

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Determining pH and Titrations

SECTION 16-2

OBJECTIVES

- Describe how an acid-base indicator functions.
- Explain how to carry out an acid-base titration.
- Calculate the molarity of a solution from titration data.

Indicators and pH Meters

An approximate value for the pH of a solution can be obtained using acid-base indicators. **Acid-base indicators** *are compounds whose colors are sensitive to pH.* In other words, the color of an indicator changes as the pH of a solution changes.

Indicators change colors because they are either weak acids or weak bases. In solution, the equilibrium of an indicator that is a weak acid can be represented by the equation below, which is modeled in Figure 16-4.

$$HIn \rightleftharpoons H^+ + In^-$$

(In^- is the symbol of the anion part of the indicator.) The colors that an indicator displays result from the fact that HIn and In^- are different colors.

In acidic solutions, any In^- ions that are present act as Brønsted bases and accept protons from the acid. The indicator is then present in largely nonionized form, HIn. The indicator has its acid-indicating color, as shown for litmus in Figure 16-4.

In basic solutions, the OH^- ions from the base combine with the H^+ ions produced by the indicator. The indicator molecules further ionize to offset the loss of H^+ ions. The indicator is thus present largely in the form of its anion, In^-. The solution now displays the base-indicating color, which for litmus is blue.

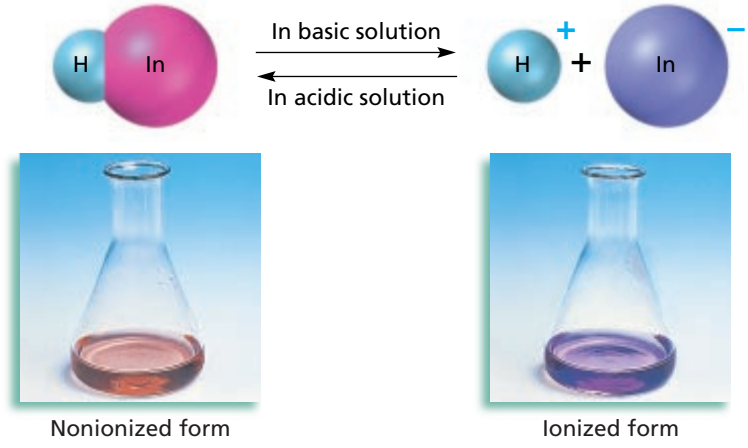

FIGURE 16-4 Basic solutions shift the equilibrium of litmus to the right. The ionized form, In^-, then predominates, and the litmus turns blue. Acidic solutions shift the equilibrium of the indicator litmus to the left. The nonionized form, HIn, predominates, and the litmus turns red.

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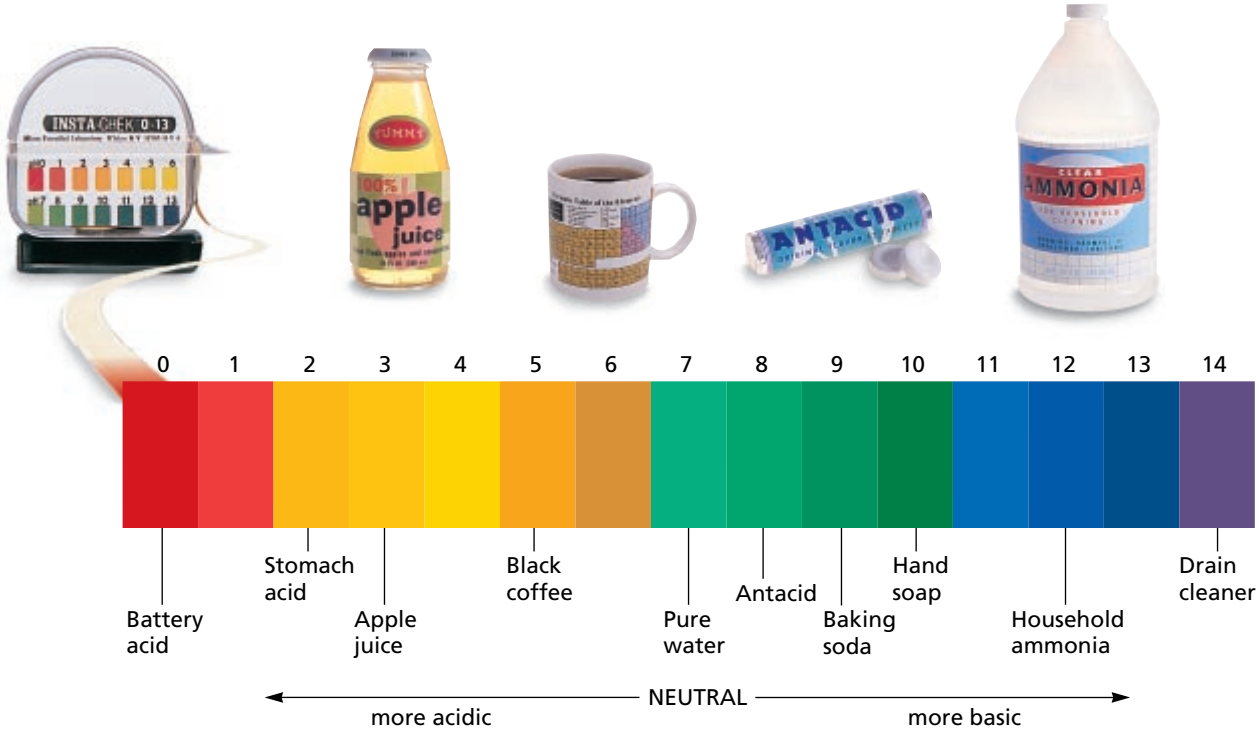

FIGURE 16-5 The pH of a solution can be determined by comparing the color it turns pH paper with the scale of the paper. The colors of pH paper at various pH values are shown, as are the pH values for some common materials.

Indicators come in many different colors. The exact pH range over which an indicator changes color also varies. *The pH range over which an indicator changes color is called its* **transition interval.** Table 16-6 gives the color changes and transition intervals for a number of common acid-base indicators.

Indicators that change color at pH lower than 7, such as methyl orange, are simply stronger acids than the other types of indicators. They tend to ionize more completely than the others. The In^- anions that these indicators produce are weaker Brønsted bases and have less tendency to accept protons from any acid being tested. These indicators therefore do not shift to their nonionized (H*In*) form unless the concentration of H^+ is fairly high. The color transition of these indicators occurs at rather low pH. In contrast, indicators that undergo transition in the higher pH range, such as phenolphthalein, are weaker acids.

Universal indicators are made by mixing several different indicators. Paper soaked in universal indicator solution is called pH paper. This paper can turn almost any color of the rainbow and provides a fairly accurate way of distinguishing the pH of solutions, as shown in Figure 16-5.

If an exact value for the pH of a solution is needed, a pH meter, shown in Figure 16-6, should be used. *A* **pH meter** *determines the pH of a solution by measuring the voltage between the two electrodes that are placed in the solution.* The voltage changes as the hydronium ion concentration in the solution changes.

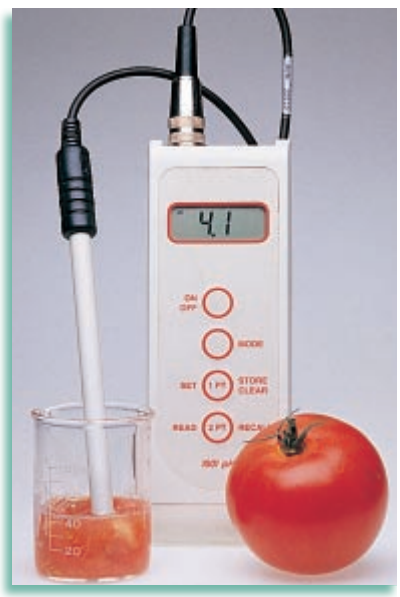

FIGURE 16-6 A pH meter measures the exact pH of a solution.

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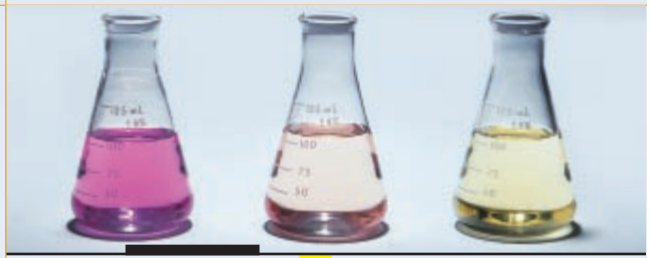
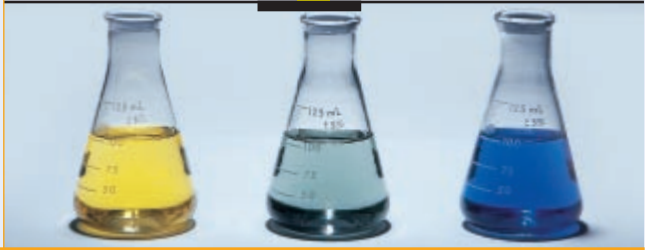
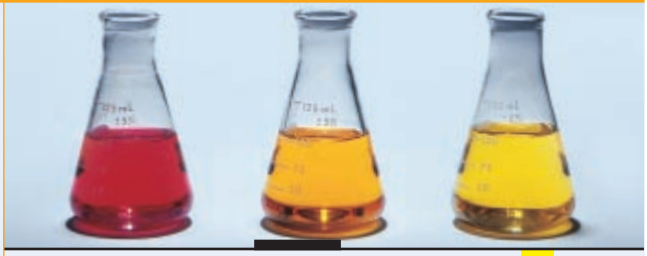
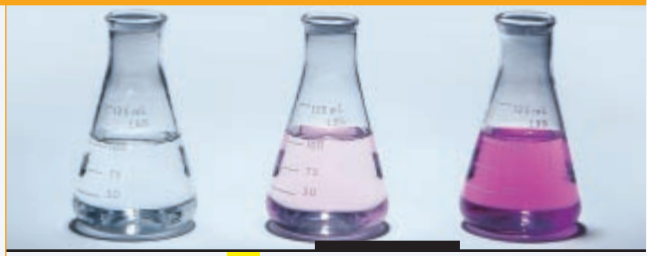
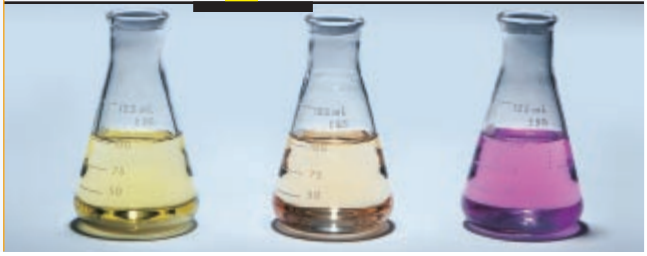
TABLE 16-6 Color Ranges of Various Indicators Used in Titrations

Titration type	Indicator	Acid color	Transition color	Base color
Strong-acid/ strong-base	methyl red (4.4–6.2)			
	bromthymol blue (6.2–7.6)			
Strong-acid/ weak-base	methyl orange (3.1–4.4)			
	bromphenol blue (3.0–4.6)			
Weak-acid/ strong-base	phenolphthalein (8.0–10.0)			
	phenol red (6.4–8.0)			

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Quick LAB

Testing the pH of Rainwater

Wear Safety Goggles and an Apron.

Materials

- rainwater
- distilled water
- 500 mL jars
- thin, transparent metric ruler (± 0.1 cm)
- pH test paper: narrow range, ± 0.2–0.3, or pH meter

Question

Do you have acid precipitation in your area?

Procedure

Record all your results in a data table.

1. Each time it rains, set out five clean jars to collect the rainwater. If the rain continues for more than 24 hours, put out new containers at the end of each 24-hour period until the rain stops. (The same procedure can be used with snow if the snow is allowed to melt before measurements are taken. You may need to use larger containers if a heavy snowfall is expected.)
2. After the rain stops or at the end of each 24-hour period, measure the depth of the water to the nearest 0.1 cm with a thin plastic ruler. Test the water with the pH paper to determine its pH to the nearest 0.2–0.3.
3. Record the following information:
   - **a.** the date and time the collection was started
   - **b.** the date and time the collection was ended
   - **c.** the location where the collection was made (town and state)
   - **d.** the amount of rainfall in centimeters
   - **e.** the pH of the rainwater
4. Find the average pH of each collection that you have made for each rainfall, and record it in the data table.
5. Collect samples on at least five different days. The more samples you collect, the more reliable your data will be.
6. For comparison, determine the pH of pure water by testing five samples of distilled water with pH paper. Record your results in a separate data table, and then calculate an average pH for distilled water.

Discussion

1. What is the pH of distilled water?
2. What is the pH of normal rainwater? How do you explain any differences between the pH readings?
3. What are the drawbacks of using a ruler to measure the depth of collected water? How could you increase the precision of your measurement?
4. Does the amount of rainfall or the time of day the sample is taken have an effect on its pH? Explain any variability among samples.
5. What conclusion can you draw from this investigation? Explain how your data support your conclusion.

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Titration

As you know, neutralization reactions occur between acids and bases. The OH^- ion acquires a proton from the H_3O^+ ion, forming two molecules of water. The following equation summarizes this reaction.

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

This equation shows that one mol of hydronium ions, 19.0 g, and one mol of hydroxide ions, 17.0 g, are chemically equivalent masses. They combine in a one-to-one ratio. Neutralization occurs when hydronium ions and hydroxide ions are supplied in equal numbers by reactants, as shown in Figure 16-7.

One liter of a 0.10 M HCl solution contains 0.10 mol of hydronium ions. Now suppose that 0.10 mol of solid NaOH is added to 1 L of 0.10 M HCl solution. The NaOH dissolves and supplies 0.10 mol of hydroxide ions to the solution. HCl and NaOH are present in chemically equivalent amounts. Hydronium and hydroxide ions, which are present in equal numbers, combine until the product $[H_3O^+]\,[OH^-]$ returns to the value of $1 \times 10^{-14}\ M^2$. NaCl, the salt produced in the reaction, is the product of the neutralization of a strong acid and a strong base. The resulting solution is neutral.

Because acids and bases react, the progressive addition of an acid to a base (or a base to an acid) can be used to compare the concentrations of the acid and the base. **Titration** *is the controlled addition and measurement of the amount of a solution of known concentration required to react completely with a measured amount of a solution of unknown concentration.* Titration provides a sensitive means of determining the chemically equivalent volumes of acidic and basic solutions.

CHEMISTRY INTERACTIVE TUTOR
Module 8: Strong and Weakly Ionized Species, pH, and Titrations

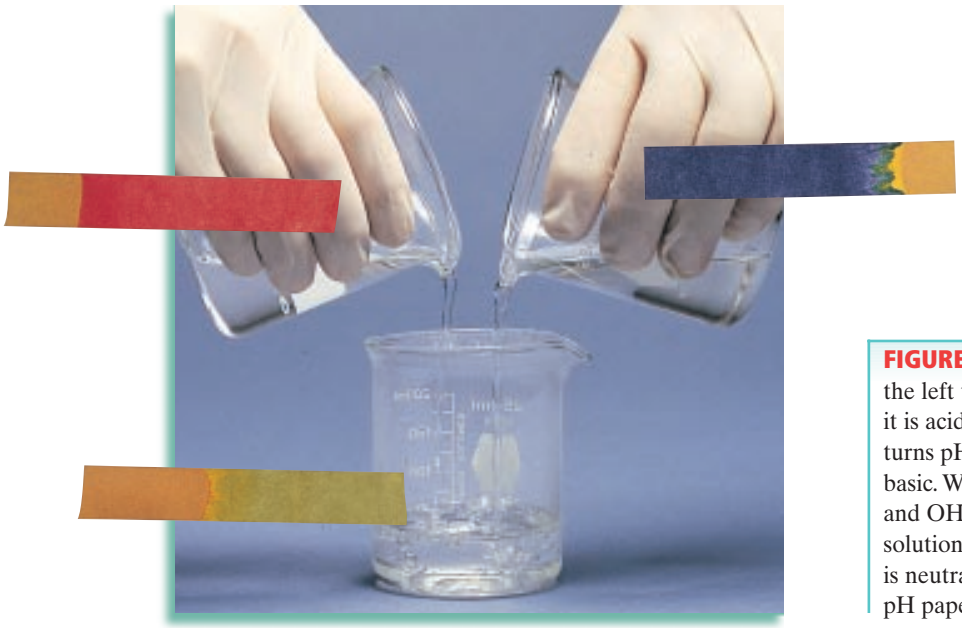

FIGURE 16-7 The solution on the left turns pH paper red because it is acidic. The solution on the right turns pH paper blue because it is basic. When equal numbers of H_3O^+ and OH^- from the acidic and basic solutions react, the resulting solution is neutral. The neutral solution turns pH paper green.

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Equivalence Point

The point at which the two solutions used in a titration are present in chemically equivalent amounts is the **equivalence point.** Indicators and pH meters can be used to determine the equivalence point. A pH meter will show a large voltage change occurring at the equivalence point. If an indicator is used, it must change color over a range that includes the pH of the equivalence point, as shown in Figure 16-8. *The point in a titration at which an indicator changes color is called the* **end point** *of the indicator.*

Some indicators, such as litmus, change color at about pH 7. However, the color-change interval for litmus is broad, pH 5.5–8.0. This broad range makes it difficult to determine an accurate pH. Bromthymol blue is better because it has a limited transition interval, pH 6.0–7.6 (see Table 16-6). Indicators that undergo transition at about pH 7 are used to determine the equivalence point of strong-acid/strong-base titrations because the neutralization of strong acids with strong bases produces a salt solution with a pH of approximately 7.

Indicators that change color at pH lower than 7 are useful in determining the equivalence point of strong-acid/weak-base titrations. Methyl orange is an example of this type. The equivalence point of a strong-acid/weak-base titration is acidic because the salt formed is itself a weak acid. Thus the salt solution has a pH lower than 7.

Indicators that change color at pH higher than 7 are useful in determining the equivalence point of weak-acid/strong-base titrations. Phenolphthalein is an example. These reactions produce salt solutions whose pH is greater than 7. This occurs because the salt formed is a weak base.

You may be wondering what type of indicator is used to determine the equivalence point of weak-acid/weak-base titrations. The surprising answer is "none at all." The pH of the equivalence point of weak acids and weak bases may be almost any value, depending on the relative strengths of the reactants. The color transition of an indicator helps

(a) (b)

FIGURE 16-8 Indicators change color at the end point of a titration. Phenolphthalein (a) turns pink and methyl red (b) turns red at the end point of these titrations.

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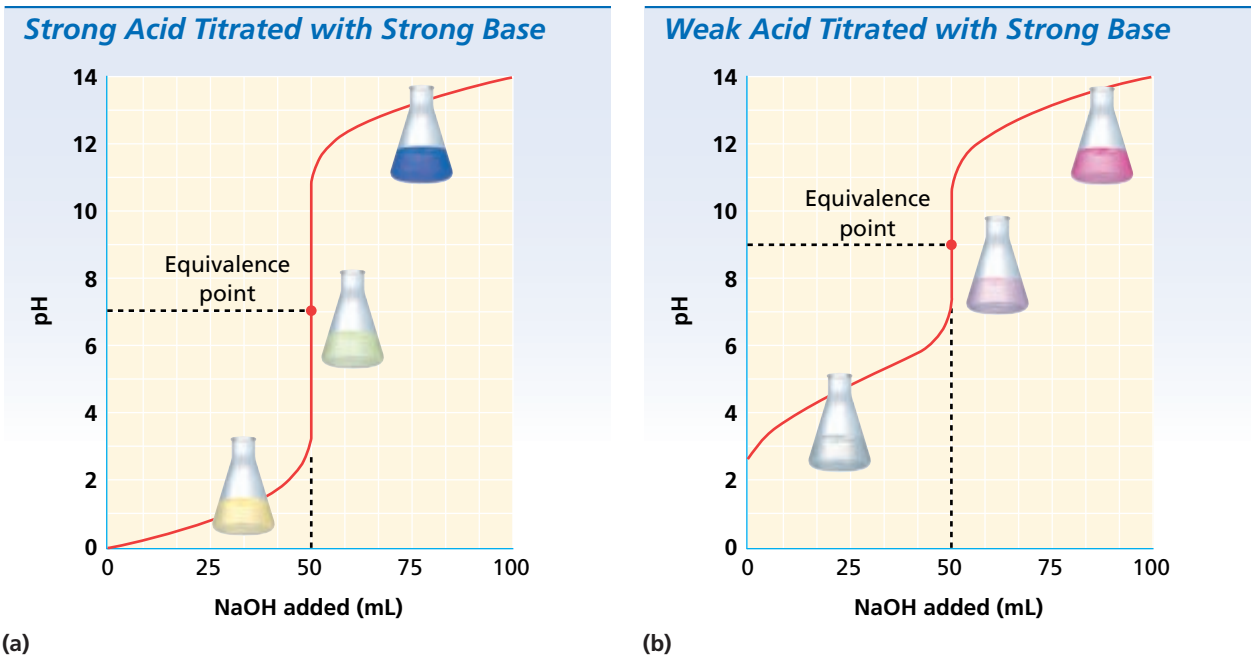

FIGURE 16-9 (a) When a strong acid, such as 50.0 mL of 1.00 M HCl, is titrated with a strong base, such as 1.00 M NaOH, the equivalence point occurs at about pH 7. (b) When a weak acid, such as 50 mL of 1.00 M CH_3COOH, is titrated with a strong base, such as 1.00 M NaOH, the equivalence point occurs at a pH above 7.

very little in determining whether reactions between such acids and bases are complete.

In a titration, successive additions of an aqueous base can be made to a measured volume of an aqueous acid. As base is added, the pH changes from a low numerical value to a high one. The change in pH occurs slowly at first, then rapidly through the equivalence point, then slowly again as the solution becomes more basic. Typical pH curves for strong-acid/strong-base and weak-acid/strong-base titrations are shown in Figure 16-9.

Molarity and Titration

Figure 16-10 on pages 500–501 shows the proper method of carrying out a titration. If the concentration of one solution is known precisely, the concentration of the other solution in a titration can be calculated from the chemically equivalent volumes. *The solution that contains the precisely known concentration of a solute is known as a* **standard solution.** It is often called simply the "known" solution.

To be certain of the concentration of the known solution, that solution must first be compared with a solution of a primary standard. *A* **primary standard** *is a highly purified solid compound used to check the concentration of the known solution in a titration.* The known solution is prepared first, and its volume is adjusted to give roughly the desired concentration. The concentration is then determined more precisely by titrating the solution with a carefully measured quantity of a solution of the primary standard.

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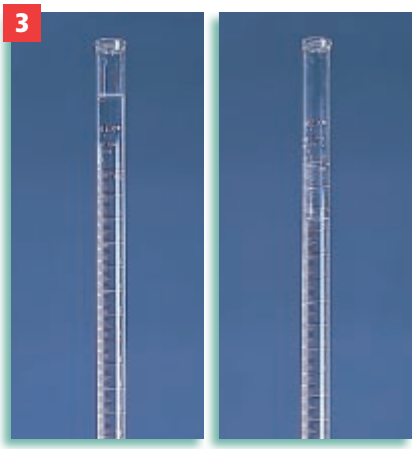
FIGURE 16-10 Following is the proper method for carrying out an acid-base titration. To be sure you have an accurate value, you should repeat the titration until you have three results that agree within 0.05 mL. This procedure would be used to determine the unknown concentration of an acid using a standardized base solution. First set up two clean burets as shown. Decide which of the burets will be used for the acid and which for the base. Rinse the acid buret three times with the acid to be used in the titration. Repeat this procedure for the base buret with the base solution to be used.

1

2

Fill the first buret to a point above the calibration mark with the acid of unknown concentration.

3



Release some acid from the buret to remove any air bubbles and to lower the volume to the calibrated portion of the buret.

4

Record the reading at the top of the acid in the buret to the nearest 0.01 mL as your starting point.

5

Release a predetermined volume of the acid (determined by your teacher or lab procedure) into a clean, dry Erlenmeyer flask.

6

Subtract the current volume reading on the buret from the initial reading. This is the exact volume of the acid released into the flask. Record it to the nearest 0.01 mL.

7

Add three drops of the appropriate indicator (in this case phenolphthalein) to the flask.

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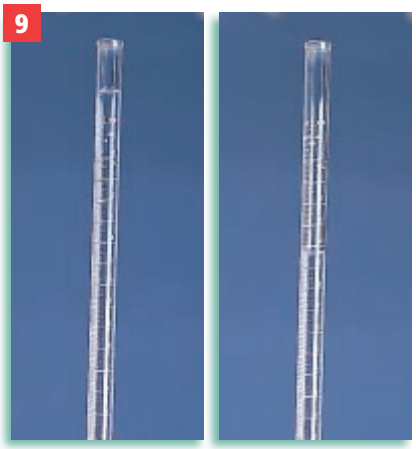
Fill the other buret with the standard base solution to a point above the calibration mark. The concentration of the standard base is known to a certain degree of precision because it was previously titrated with an exact mass of solid acid.

8

9



Release some base from the buret to remove any air bubbles and to lower the volume to the calibrated portion of the buret.

10

Record the reading at the top of the base to the nearest 0.01 mL as your starting point.

11

Place the Erlenmeyer flask under the base buret as shown. Notice that the tip of the buret extends into the mouth of the flask.

12

Slowly release base from the buret into the flask while constantly swirling the contents of the flask. The pink color of the indicator should fade with swirling.

13

The titration is nearing the end point when the pink color stays for longer periods of time. At this point, add base drop by drop.

14

The equivalence point is reached when a very light pink color remains after 30 seconds of swirling.

15

Subtract the current volume reading on the buret from the initial reading. This is the exact volume of the base released into the flask. Record it to the nearest 0.01 mL.

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The known solution can be used to determine the molarity of another solution by titration. Suppose 20.0 mL of 5.0×10^{-3} M NaOH is required to reach the end point in the titration of 10.0 mL of HCl of unknown concentration. How can these titration data be used to determine the molarity of the acidic solution?

Begin with the balanced neutralization reaction equation. From the equation, determine the chemically equivalent amounts of HCl and NaOH.

$$\underset{1\text{ mol}}{HCl(aq)} + \underset{1\text{ mol}}{NaOH(aq)} \longrightarrow \underset{1\text{ mol}}{NaCl(aq)} + \underset{1\text{ mol}}{H_2O(l)}$$

Calculate the number of moles of NaOH used in the titration.

$$\frac{5.0 \times 10^{-3}\text{ mol NaOH}}{\cancel{L}} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times 20.0\ \cancel{mL} = 1.0 \times 10^{-4}\text{ mol NaOH used}$$

Because 1 mol of NaOH is needed to neutralize 1 mol of HCl, the amount of HCl in the titration must be 1.0×10^{-4} mol. This is confirmed by the following equation.

$$1.0 \times 10^{-4}\ \cancel{\text{mol NaOH}} \times \frac{1\text{ mol HCl}}{1\ \cancel{\text{mol NaOH}}} = 1.0 \times 10^{-4}\text{ mol HCl}$$

This amount of acid must be in the 10.0 mL of the HCl solution used for the titration. The molarity of the HCl solution can now be calculated.

$$\frac{1 \times 10^{-4}\text{ mol HCl}}{10.0\ \cancel{mL}} \times \frac{1000\ \cancel{mL}}{1\text{ L}} = \frac{1.0 \times 10^{-2}\text{ mol HCl}}{\text{L}}$$

$$= 1.0 \times 10^{-2}\text{ M HCl}$$

Sample Problem 16-6 illustrates the following four steps.

1. Start with the balanced equation for the neutralization reaction, and determine the chemically equivalent amounts of the acid and base.
2. Determine the moles of acid (or base) from the known solution used during the titration.
3. Determine the moles of solute of the unknown solution used during the titration.
4. Determine the molarity of the unknown solution.

SAMPLE PROBLEM 16-6

In a titration, 27.4 mL of 0.0154 M $Ba(OH)_2$ is added to a 20.0 mL sample of HCl solution of unknown concentration. What is the molarity of the acid solution?

SOLUTION

1 ANALYZE

Given: volume and concentration of known solution = 27.4 mL of 0.0154 M $Ba(OH)_2$
volume of unknown HCl solution = 20.0 mL

Unknown: molarity of acid solution

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2 PLAN

1. balanced neutralization equation ⟶ chemically equivalent amounts

$$\underset{1\text{ mol}}{Ba(OH)_2} + \underset{2\text{ mol}}{2HCl} \longrightarrow \underset{1\text{ mol}}{BaCl_2} + \underset{2\text{ mol}}{2H_2O}$$

2. volume of known basic solution used (mL) ⟶ amount of base used (mol)

$$\frac{\text{mol Ba(OH)}_2}{\text{L}} \times \text{mL of Ba(OH)}_2\text{ solution} \times \frac{1\text{ L}}{1000\text{ mL}} = \text{mol Ba(OH)}_2$$

3. mole ratio, moles of base used ⟶ moles of acid used from unknown solution

$$\frac{2\text{ mol HCl}}{1\text{ mol Ba(OH)}_2} \times \text{mol Ba(OH)}_2\text{ in known solution} = \text{mol HCl in unknown solution}$$

4. volume of unknown, moles of solute in unknown ⟶ molarity of unknown

$$\frac{\text{amount of solute in unknown solution (mol)}}{\text{volume of unknown solution (mL)}} \times \frac{1000\text{ mL}}{1\text{ L}} = \text{molarity of unknown solution}$$

3 COMPUTE

1. The mole ratio from the equation is 1 mol $Ba(OH)_2$ for every 2 mol HCl.

2. $\dfrac{0.0154\text{ mol Ba(OH)}_2}{\cancel{\text{L}}} \times 27.4\ \cancel{\text{mL}} \times \dfrac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} = 4.22 \times 10^{-4}\text{ mol Ba(OH)}_2$

3. $\dfrac{2\text{ mol HCl}}{1\ \cancel{\text{mol Ba(OH)}_2}} \times 4.22 \times 10^{-4}\ \cancel{\text{mol Ba(OH)}_2} = 8.44 \times 10^{-4}\text{ mol HCl}$

4. $\dfrac{8.44 \times 10^{-4}\text{ mol HCl}}{20.0\ \cancel{\text{mL}}} \times \dfrac{1000\ \cancel{\text{mL}}}{1\text{ L}} = \dfrac{4.22 \times 10^{-2}\text{ mol HCl}}{\text{L}} = 4.22 \times 10^{-2}\text{ M HCl}$

PRACTICE

1. A 15.5 mL sample of 0.215 M KOH solution required 21.2 mL of aqueous acetic acid solution in a titration experiment. Calculate the molarity of the acetic acid solution.

   Answer
   0.157 M CH_3COOH

2. By titration, 17.6 mL of aqueous H_2SO_4 neutralized 27.4 mL of 0.0165 M LiOH solution. What was the molarity of the aqueous acid solution?

   Answer
   0.0128 M H_2SO_4

SECTION REVIEW

1. Name an appropriate indicator for titrating the following:
   a. a strong acid and a weak base
   b. a strong base and a weak acid
2. Suppose you have an NaOH solution of unknown concentration. Name three possible substances that could be used in "known" solutions to titrate the NaOH solution.
3. If 20.0 mL of 0.0100 M aqueous HCl is required to neutralize 30.0 mL of an aqueous solution of NaOH, determine the molarity of the NaOH solution.
4. Suppose that 20.0 mL of 0.10 M $Ca(OH)_2$ is required to neutralize 12.0 mL of aqueous HCl solution. What is the molarity of the HCl solution?

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CHAPTER 16 REVIEW

CHAPTER SUMMARY

16-1

- Pure water undergoes self-ionization to give 1.0×10^{-7} M H_3O^+ and 1.0×10^{-7} M OH^- at 25°C.
- $pH = -\log[H_3O^+]$; $pOH = -\log[OH^-]$
  At 25°C, pH + pOH = 14.0.
- At 25°C, acids have a pH of less than 7, bases have a pH of greater than 7, and neutral solutions have a pH of 7.
- If a solution contains a strong acid or a strong base, the $[H_3O^+]$, $[OH^-]$ and pH can be calculated from the molarity of the solution. If a solution contains a weak acid or a weak base, the $[H_3O^+]$ and the $[OH^-]$ must be calculated from an experimentally measured pH.

Vocabulary

pH (485) pOH (485) self-ionization of water (481)

16-2

- The pH of a solution can be determined using either a pH meter or acid-base indicators.
- Titration uses a solution of known concentration to determine the concentration of a solution of unknown concentration.
- To determine the end point of a titration, indicators are chosen that change color over ranges that include the pH of the equivalence point.
- When the molarity and volume of a known solution used in a titration are known, then the molarity of a given volume of an unknown solution can be found.

Vocabulary

end point (498) acid-base indicators (493) primary standard (499) titration (497)
equivalence point (498) pH meter (494) standard solution (499) transition interval (494)

REVIEWING CONCEPTS

1. Why does pure water weakly conduct an electric current? (16-1)

2. What does it mean when the formula of a particular ion or molecule is enclosed in brackets? (16-1)

3. a. What is the $[H_3O^+]$ of pure water at 25°C?
b. Is this true at all temperatures? Why or why not? (16-1)

4. a. What is always true about the $[H_3O^+]$ value of acidic solutions?
b. What is true about the $[H_3O^+]$ value of acidic solutions at 25°C? (16-1)

5. a. Describe what is meant by the pH of a solution.
b. Write the equation for determining pH.
c. Explain and illustrate what is meant by the common logarithm of a number. (16-1)

6. Identify each of the following as being true of acidic, basic, or neutral solutions at 25°C:
a. $[H_3O^+] = 1.0 \times 10^{-7}$ M
b. $[H_3O^+] = 1.0 \times 10^{-10}$ M
c. $[OH^-] = 1.0 \times 10^{-7}$ M
d. $[OH^-] = 1.0 \times 10^{-11}$ M
e. $[H_3O^+] = [OH^-]$
f. pH = 3.0
g. pH = 13.0 (16-1)

7. Arrange the following common substances in order of increasing pH:
a. eggs
b. apples
c. tomatoes
d. milk
e. bananas
f. potatoes
g. lemons
h. milk of magnesia
i. sea water (16-1)

8. What is meant by the transition interval of an indicator? (16-2)

9. Explain how an indicator's equilibrium determines the color the indicator displays at a given pH. (16-2)

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10. a. Other than through indicators, how can the equivalence point of a titration experiment or the pH of a solution be determined?
b. What can be observed about the rate of change in the pH of a solution near the end point of a titration? (16-2)

11. a. What is meant by the end point of a titration?
b. What is the role of an indicator in the titration process?
c. On what basis is an indicator selected for a particular titration experiment? (16-2)

12. For each of the four possible types of acid-base titration combinations, indicate the approximate pH at the end point. Also name a suitable indicator for detecting that end point. (16-2)

13. Based on Figures 14-9(a) and 14-9(b), draw a pH curve for a strong-acid/weak-base titration. (16-2)

14. An unknown solution is colorless when tested with phenolphthalein but causes the indicator phenol red to turn red. Based on this information, what is the approximate pH of this solution? (16-2)

PROBLEMS

pH Calculations

15. Calculate the $[H_3O^+]$ and $[OH^-]$ for each of the following. (Hint: See Sample Problem 16-1.)
a. 0.03 M HCl
b. 1×10^{-4} M NaOH
c. 5×10^{-3} M H_2SO_4
d. 0.01 M $Ca(OH)_2$

16. Determine the pH of each of the following solutions. (Hint: See Sample Problem 16-2.)
a. 1.0×10^{-2} M HCl
b. 1.0×10^{-3} M HNO_3
c. 1.0×10^{-5} M HI
d. 1.0×10^{-4} M HBr

17. Given the following $[OH^-]$ values, determine the pH of each solution.
a. 1.0×10^{-6} M
b. 1.0×10^{-9} M
c. 1.0×10^{-2} M
d. 1.0×10^{-7} M

18. Determine the pH of each solution.
a. 1.0×10^{-2} M NaOH
b. 1.0×10^{-3} M KOH
c. 1.0×10^{-4} M LiOH

19. Determine the pH of solutions with each of the following $[H_3O^+]$. (Hint: See Sample Problem 16-3.)
a. 2.0×10^{-5} M
b. 4.7×10^{-7} M
c. 3.8×10^{-3} M

20. Given the following pH values, determine the $[H_3O^+]$ for each solution. (Hint: See Sample Problem 16-4.)
a. 3.0
b. 7.00
c. 11.0
d. 5.0

21. Given the following pH values, determine the $[OH^-]$ for each solution.
a. 7.00
b. 11.00
c. 4.00
d. 6.00

22. Determine $[H_3O^+]$ for solutions with the following pH values. (Hint: See Sample Problem 16-5.)
a. 4.23 b. 7.65 c. 9.48

23. A nitric acid solution is found to have a pH of 2.70. Determine each of the following:
a. $[H_3O^+]$
b. $[OH^-]$
c. the number of moles of HNO_3 required to prepare 5.50 L of this solution
d. the mass of the moles of HNO_3 in the solution in part (c)
e. the milliliters of concentrated acid needed to prepare the solution in part (c) (Concentrated nitric acid is 69.5% HNO_3 by mass and has a density of 1.42 g/mL.)

Titrations

24. For each of the following acid-base titration combinations, determine the number of moles of the first substance listed that would be the chemically equivalent amount of the second substance.
a. NaOH with 1.0 mol HCl
b. HNO_3 with 0.75 mol KOH
c. $Ba(OH)_2$ with 0.20 mol HF
d. H_2SO_4 with 0.60 mol $Al(OH)_3$

25. Suppose that 15.0 mL of 2.50×10^{-2} M aqueous H_2SO_4 is required to neutralize 10.0 mL of an aqueous solution of KOH. What is the molarity of the KOH solution? (Hint: See Sample Problem 16-6.)

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26. In a titration experiment, a 12.5 mL sample of 1.75×10^{-2} M $Ba(OH)_2$ just neutralized 14.5 mL of HNO_3 solution. Calculate the molarity of the HNO_3 solution.

MIXED REVIEW

27. a. What is the $[OH^-]$ of a 4.0×10^{-4} M solution of $Ca(OH)_2$?
b. What is the $[H_3O^+]$ of the solution?

28. Given the following $[H_3O^+]$ values, determine the pH of each solution.
a. 1.0×10^{-7} M
b. 1.0×10^{-3} M
c. 1.0×10^{-12} M
d. 1.0×10^{-5} M

29. What is the $[H_3O^+]$ for a solution that has a pH of 6.0?

30. Suppose that a 5.0×10^{-5} M solution of $Ba(OH)_2$ is prepared. What is the pH of the solution?

31. a. Calculate the pH of a solution that has an $[H_3O^+]$ of 8.4×10^{-11} M.
b. Calculate the $[H_3O^+]$ of a solution that has a pH of 2.50.

32. a. What is the concentration of OH^- in a 5.4×10^{-5} M solution of magnesium hydroxide, $Mg(OH)_2$?
b. Calculate the concentration of H_3O^+ for this solution.

33. a. Calculate the molarity of H_3O^+ in a solution that has a pH of 8.90.
b. Calculate the concentration of OH^- in the solution.

34. What is the pH of a solution for which $[OH^-]$ equals 6.9×10^{-10} M?

35. In a titration, 25.9 mL of 3.4×10^{-3} M $Ba(OH)_2$ neutralized 16.6 mL of HCl solution. What is the molarity of the HCl solution?

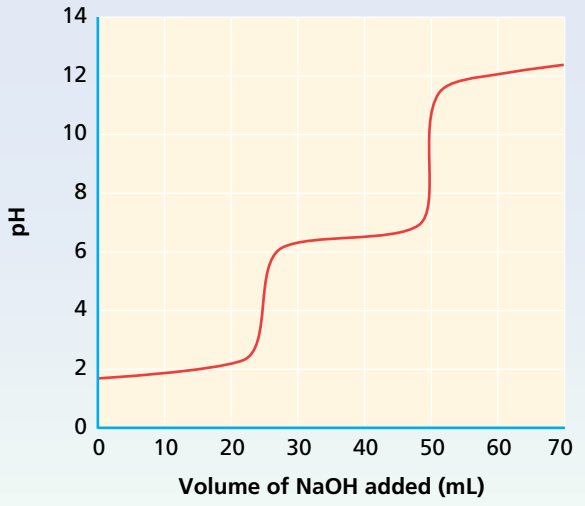
36. Find the molarity of a $Ca(OH)_2$ solution, given that 428 mL of it is neutralized in a titration by 115 mL of 6.7×10^{-3} M HNO_3.

37. Suppose that 10.1 mL of HNO_3 is neutralized by 71.4 mL of a 4.2×10^{-3} M solution of KOH in a titration. Calculate the concentration of the HNO_3 solution.

CRITICAL THINKING

38. Interpreting Graphics The following titration curve resulted from the titration of an unknown acid with 0.10 M NaOH. Analyze the curve. Make inferences related to the type of acidic solution titrated.

Titration of an Unknown Acid



TECHNOLOGY & LEARNING

39. Graphing Calculator Graphing Titration Data

The graphing calculator can run a program that graphs data such as pH versus volume of base. Graphing the titration data will allow you to determine which combination of acid and base is represented by the shape of the graph. Begin by creating a table of data. Then program the calculator to plot the data.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that after creating your lists, you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

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a. At what approximate volume does the titration change from acidic to basic?
b. What would you expect the pH to be for a titration with a volume of 70 mL?
c. At what volume would you expect the titration to become purely acidic?

HANDBOOK SEARCH

40. The normal pH of blood is about 7.4. When the pH shifts above or below that level, the results are acidosis or alkalosis. Review the section on blood pH in Group 14 of the *Elements Handbook,* then answer the following.
a. What chemical species keep H_3O^+ in blood at the appropriate pH?
b. What condition results when there is an excess of CO_2 in the blood?
c. What is hyperventilation and how does it affect blood pH?

RESEARCH & WRITING

41. Examine the labels of at least five brands of shampoo. Note what is written there, if anything, regarding the pH of the shampoo. Do library research to find out why such pH ranges are chosen and why other ranges might be harmful to hair or eyes.

42. Water quality depends on the ability of treatment facilities to reprocess waste water. Most waste-water treatment facilities use living organisms to break down wastes. Because of acid rain, the acidic nature of waste water can pose problems for a waste-treatment plant. Conduct library research on this topic and write a brief report. Include a description of how the low pH of acidic waste water can affect the ecology of a waste-water treatment plant.

ALTERNATIVE ASSESSMENT

43. Performance Use pH paper to determine the approximate pH of various brands of orange juice, which contains citric acid.

44. Performance Design and conduct an experiment to extract possible acid-base indicators from sources such as red cabbage, berries, and flower petals. Use known acidic, basic, and neutral solutions to test the action of each indicator that you are able to isolate.

45. Performance Design and conduct an experiment to study the pH of rain for an extended period of time. Coordinate your data-collection activities with those of your classmates so that the pH readings are made in a variety of locations. Try to determine whether any patterns emerge in terms of location, season, time of day, degree of industrialization in the area, and so on.

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CHAPTER 17

Reaction Energy and Reaction Kinetics

Many chemical reactions give off or take in energy as heat.

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Thermochemistry

SECTION 17-1

Objectives

- Define *temperature* and state the units in which it is measured.
- Define *heat* and state its units.
- Perform specific-heat calculations.
- Explain heat of reaction, heat of formation, heat of combustion, and enthalpy change.
- Solve problems involving heats of reaction, heats of formation, and heats of combustion.

Virtually every chemical reaction is accompanied by a change in energy. Chemical reactions usually absorb or release energy as heat. You learned in Chapter 12 that heat is also absorbed or released in physical changes, such as melting a solid or condensing a vapor. **Thermochemistry** *is the study of the transfers of energy as heat that accompany chemical reactions and physical changes.*

Heat and Temperature

The energy absorbed or released as heat in a chemical or physical change is measured in a **calorimeter.** In one kind of calorimeter, known quantities of reactants are sealed in a reaction chamber, which is immersed in a known quantity of water in an insulated vessel. Therefore, the energy given off (or absorbed) during the reaction is equal to the energy absorbed (or given off) by the known quantity of water. The amount of energy is determined from the temperature change of the known mass of surrounding water. The data collected from calorimetry experiments are temperature changes because heat cannot be measured directly; but temperature, which is affected by the transfer of energy as heat, is directly measurable. To see why this is so, let us look at the definitions of heat and temperature and at how temperature is measured.

Temperature *is a measure of the average kinetic energy of the particles in a sample of matter.* The greater the kinetic energy of the particles in a sample, the higher the temperature and the hotter it feels. To assign a numerical value to temperature, it is necessary to define a temperature scale. For calculations in thermochemistry, we use the Celsius and Kelvin scales. A Celsius temperature can be converted to Kelvin temperature by adding 273.15, although in most calculations in this book, it is acceptable to add 273.

The ability to measure temperature is thus based on heat transfer. The amount of energy transferred as heat is usually measured in joules. *A* **joule** *is the SI unit of heat as well as all other forms of energy*. The joule, abbreviated J, is derived from the units for force and length.

$$N \times m = \frac{kg \times m^2}{s^2}$$

Because the joule is a rather small unit compared with other units for heat, the kilojoule, kJ, is also commonly used as a unit for heat.

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FIGURE 17-1 The direction of energy transfer is determined by the temperature differences between the objects within a system. The energy is transferred as heat from the hotter brass bar to the cooler water. This energy transfer will continue until the bar and the water reach the same temperature.

Heat *can be thought of as the energy transferred between samples of matter because of a difference in their temperatures*. Energy transferred as heat always moves spontaneously from matter at a higher temperature to matter at a lower temperature, as shown in Figure 17-1. The temperature of the cool water in the beaker increases as energy flows into it. Likewise, the temperature of the hot brass bar decreases as energy flows away from it. When the temperature of the water equals the temperature of the brass bar, energy is no longer transferred as heat within the system.

Heat Capacity and Specific Heat

The quantity of energy transferred as heat during a temperature change depends on the nature of the material changing temperature, the mass of the material changing temperature, and the size of the temperature change. One gram of iron heated to 100.0°C and cooled to 50.0°C in a calorimeter transfers 22.5 J of energy to the surrounding water. But one gram of silver transfers 11.8 J of energy under the same conditions. The difference results from the metals' differing capacities for absorbing this energy. A quantity called specific heat can be used to compare heat absorption capacities for different materials. **Specific heat** *is the amount of energy required to raise the temperature of one gram of substance by one Celsius degree (1°C) or one kelvin (1 K)*(because the sizes of the degree divisions on both scales are equal). Values of specific heat can be given in units of joules per gram per Celsius degree, J/(g•°C), joules per gram per kelvin, J/(g•K), or calories per gram per Celsius degree, cal/(g•°C). Table 17-1 gives the specific heats of some common substances. Notice the extremely high specific heat of water, one of the highest of most common substances.

Specific heat is usually measured under constant pressure conditions, so its symbol, c_p, contains a subscripted p as a reminder to the reader.

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TABLE 17-1 Specific Heats of Some Common Substances at 298.15 K

Substance	Specific heat J/(g•K)
Water (*l*)	4.18
Water (*s*)	2.06
Water (*g*)	1.87
Ammonia (*g*)	2.09
Benzene (*l*)	1.74
Ethanol (*l*)	2.44
Ethanol (*g*)	1.42
Aluminum (*s*)	0.897
Calcium (*s*)	0.647
Carbon, graphite (*s*)	0.709
Copper (*s*)	0.385
Gold (*s*)	0.129
Iron (*s*)	0.449
Mercury (*l*)	0.140
Lead (*s*)	0.129

In the following mathematical equation, c_p is the specific heat at a given pressure, q is the energy lost or gained, m is the mass of the sample, and ΔT represents the difference between the initial and final temperatures.

$$c_p = \frac{q}{m \times \Delta T}$$

This equation can be rearranged to give an equation that can be used to find the quantity of energy gained or lost with a change in temperature.

$$q = c_p \times m \times \Delta T$$

SAMPLE PROBLEM 17-1

A 4.0 g sample of glass was heated from 274 K to 314 K, a temperature increase of 40 K, and was found to have absorbed 32 J of energy as heat.
a. What is the specific heat of this type of glass?
b. How much energy will the same glass sample gain when it is heated from 314 K to 344 K?

SOLUTION

1 *ANALYZE*

Given: $m = 4.0$ g
$\Delta T = 40$ K
$q = 32$ J

Unknown: c_p in J/(g•K)

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2 PLAN

a. The specific heat, c_p, of the glass is calculated using the equation given for specific heat.

$$c_p = \frac{q}{m \times \Delta T}$$

b. The rearranged specific heat equation is used to find the energy gained when the glass was heated.

$$q = c_p \times m \times \Delta T$$

3 COMPUTE

a. $$\frac{32\ \text{J}}{(4.0\ \text{g})(40\ \text{K})} = 0.20\ \text{J/(g•K)}$$

b. $$\frac{0.20\ \text{J}}{(\text{g•K})}(4.0\ \text{g})(71\ \text{K} - 41\ \text{K})$$

$$\frac{0.20\ \text{J}}{(\text{g•K})}(4.0\ \text{g})(30\ \text{K}) = 24\ \text{J}$$

4 EVALUATE

The units combine or cancel correctly to give the specific heat in J/(g•K) and the energy in J. Both answers are correct given to two significant figures.

PRACTICE

1. Determine the specific heat of a material if a 35 g sample absorbed 48 J as it was heated from 293 K to 313 K.

Answer
0.069 J/(g•K)

2. If 980 kJ of energy are added to 6.2 L of water at 291 K, what will the final temperature of the water be?

Answer
329 K

Heat of Reaction

The **heat of reaction** *is the quantity of energy released or absorbed as heat during a chemical reaction.* You can think of heat of reaction as the difference between the stored energy of the reactants and the products.

If a mixture of hydrogen and oxygen is ignited, water will form and energy will be released explosively. The energy that is released comes from the reactants as they form products. Because energy is released, the reaction is exothermic, and the energy of the product, water, must be less than the energy of the reactants before ignition. The following chemical equation for this reaction indicates that when 2 mol of hydrogen gas at room temperature are burned, 1 mol of oxygen gas is consumed and 2 mol of water vapor are formed.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The equation does not tell you that energy is evolved as heat during the reaction. Experiments have shown that 483.6 kJ of energy are evolved when 2 mol of gaseous water are formed at 298.15 K from its elements.

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Modifying the chemical equation to show the amount of energy produced during the reaction gives the following expression.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) + 483.6\ kJ$$

This expression is an example of a **thermochemical equation,** *an equation that includes the quantity of energy released or absorbed as heat during the reaction as written.* In any thermochemical equation, we must always interpret the coefficients as *numbers of moles* and never as *numbers of molecules.* The quantity of energy released as heat in this or any reaction depends on the amounts of reactants and products. The quantity of energy released during the formation of water from H_2 and O_2 is proportional to the quantity of water formed. Producing twice as much water vapor would require twice as many moles of reactants and would release 2×483.6 kJ of energy as heat, as shown in the following thermochemical equation.

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(g) + 967.2\ kJ$$

Producing one-half as much water would require one-half as many moles of reactants and would release only one-half as much energy, or $1/2 \times 483.6$ kJ. The thermochemical equation for this reaction follows.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) + 241.8\ kJ$$

Fractional coefficients are sometimes used in thermochemical equations.

The situation is reversed in an endothermic reaction because products have a higher energy than reactants. The decomposition of water vapor is endothermic; it is the reverse of the reaction that forms water vapor. The amount of energy absorbed by water molecules to form hydrogen and oxygen equals the amount of energy released when the elements combine to form the water. This is to be expected because the difference between the energy of reactants and products is unchanged. Energy now appears on the reactant side of the thermochemical equation that follows, indicating that it was absorbed during the reaction.

$$2H_2O(g) + 483.6\ kJ \longrightarrow 2H_2(g) + O_2(g)$$

The physical states of reactants and products must always be included in thermochemical equations because they influence the overall amount of energy exchanged. For example, the energy needed for the decomposition of water would be greater than 483.6 kJ if we started with ice because extra energy would be needed to melt the ice and to change the liquid into a vapor.

The energy absorbed or released as heat during a chemical reaction at constant pressure is represented by ΔH. The H is the symbol for a quantity called *enthalpy.* Enthalpy has traditionally been defined as the heat content of a system at constant pressure. However, the term "heat content" is misleading. Also, it is not practical to talk just about enthalpy as a quantity, because we have no way to directly measure the enthalpy of a system. Only *changes* in enthalpy can be measured. The Greek

CHEMISTRY INTERACTIVE TUTOR
Module 9: Thermochemistry

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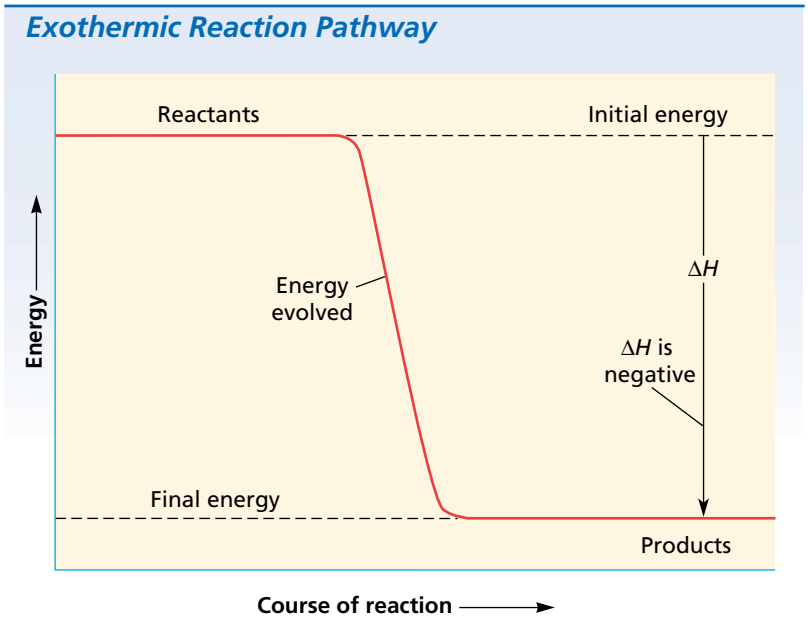

FIGURE 17-2 In an exothermic chemical reaction, the enthalpy change is negative, meaning energy is released from the system as heat.

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letter Δ (a capital "delta") stands for "change in." Therefore, ΔH is read as "change in enthalpy." *An* **enthalpy change** *is the amount of energy absorbed or lost by a system as heat during a process at constant pressure.* The enthalpy change is always the difference between the enthalpies of the products and the reactants. The following equation expresses an enthalpy change mathematically.

$$\Delta H = H_{products} - H_{reactants}$$

Thermochemical equations are usually written by designating the value of ΔH rather than writing the energy as a reactant or product. By convention, for an exothermic reaction, ΔH is always given a minus sign because the system loses energy. So the thermochemical equation for the exothermic formation of 2 mol of gaseous water from its elements now has the following form.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \quad \Delta H = -483.6 \text{ kJ/mol}$$

Figure 17-2 graphically shows the course of an exothermic reaction. The initial energy of the reactants is greater than the final energy of the products. This means energy is evolved, or given off, during the reaction; this is described as a negative enthalpy change.

For an endothermic reaction, ΔH is always given a positive value because the system gains energy. Thus, the endothermic decomposition of 2 mol of gaseous water has the following thermochemical equation.

$$2H_2O(g) \longrightarrow 2H_2(g) + O_2(g) \quad \Delta H = +483.6 \text{ kJ/mol}$$

The course of an endothermic reaction is illustrated in Figure 17-3.

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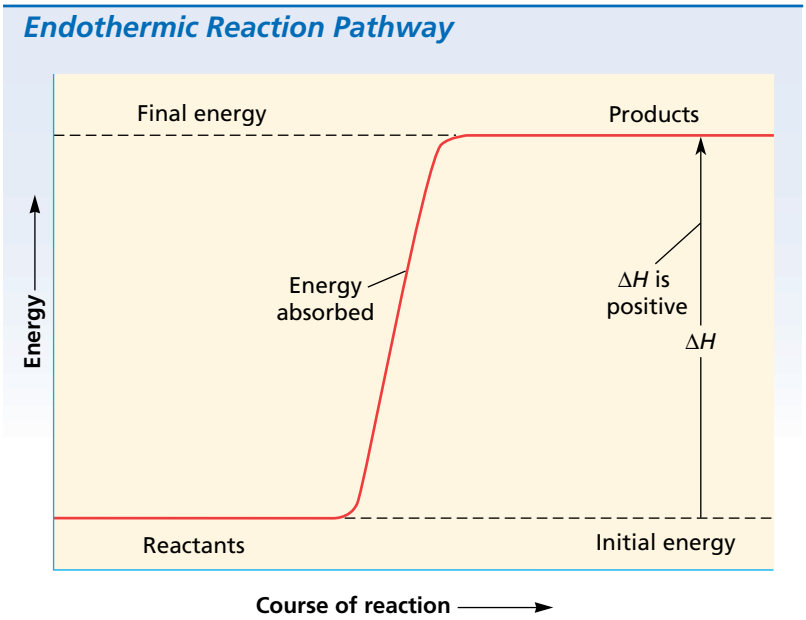

FIGURE 17-3 In an endothermic chemical reaction, the enthalpy change is positive because energy is absorbed into the system as heat.

Energy is absorbed in this reaction, meaning that the initial energy of the reactants is lower than the final energy of the products. In this case, ΔH is designated as positive.

Keep in mind the following concepts when using thermochemical equations.

1. The coefficients in a balanced thermochemical equation represent the numbers of *moles* of reactants and products and never the numbers of *molecules*. This allows us to write these coefficients as fractions rather than whole numbers when necessary.
2. The physical state of the product or reactant involved in a reaction is an important factor and therefore must be included in the thermochemical equation.
3. The change in energy represented by a thermochemical equation is directly proportional to the number of moles of substances undergoing a change. For example, if 2 mol of water are decomposed, twice as much energy, 483.6 kJ, is needed than for the decomposition of 1 mol of water.
4. The value of the energy change, ΔH, is usually not significantly influenced by changing temperature.

Heat of Formation

The formation of water from hydrogen and oxygen is a composition reaction—the formation of a compound from its elements. Thermochemical data are often recorded as the heats of such composition reactions. *The* **molar heat of formation** *is the energy released or absorbed as heat when one mole of a compound is formed by combination of its elements.*

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To make comparisons meaningful, heats of formation are given for the standard states of reactants and products—these are the states found at atmospheric pressure and, usually, room temperature (298.15 K). Thus, the standard state of water is liquid, not gas or solid. The standard state of iron is solid, not a molten liquid. To signify that a value represents measurements on substances in their standard states, a ^{0} sign is added to the enthalpy symbol, giving ΔH^0 for the standard heat of a reaction. Adding a subscript *f*, as in ΔH_f^0, further indicates a standard heat of formation.

Some standard heats of formation are given in Appendix Table A-14 (page 902). Each entry in the table is the heat of formation for the synthesis of *one mole* of the compound listed from its elements in their standard states. The thermochemical equation to accompany each heat of formation shows the formation of one mole of the compound from its elements in their standard states.

Stability and Heat of Formation

If a large amount of energy is released when a compound is formed, the compound has a high negative heat of formation. Such compounds are very stable. Once they start, the reactions forming them usually proceed vigorously and without outside assistance.

Elements in their standard states are *defined* as having $\Delta H_f^0 = 0$. The ΔH_f^0 of carbon dioxide is –393.5 kJ/mol of gas produced. Therefore, carbon dioxide is more stable than the elements from which it was formed. You can see in Appendix Table A-14 (page 902) that the majority of the heats of formation are negative.

Compounds with relatively positive values of heats of formation, or only slightly negative values, are relatively unstable and will spontaneously decompose into their elements if the conditions are appropriate. Hydrogen iodide, HI, is a colorless gas that decomposes somewhat when stored at room temperature. It has a relatively high positive heat of formation of +26.5 kJ/mol. As it decomposes, violet iodine vapor becomes visible throughout the container of the gas.

Compounds with a high positive heat of formation are sometimes very unstable and may react or decompose violently. For example, ethyne (acetylene), C_2H_2, (ΔH_f^0 = +226.7 kJ/mol) reacts violently with oxygen and must be stored in cylinders as a solution in acetone. Mercury fulminate, $HgC_2N_2O_2$, has a very high heat of formation of +270 kJ/mol. Its instability makes it useful as a detonator for explosives.

Heat of Combustion

Combustion reactions produce a considerable amount of energy in the form of light and heat when a substance is combined with oxygen. *The energy released as heat by the complete combustion of one mole of a*

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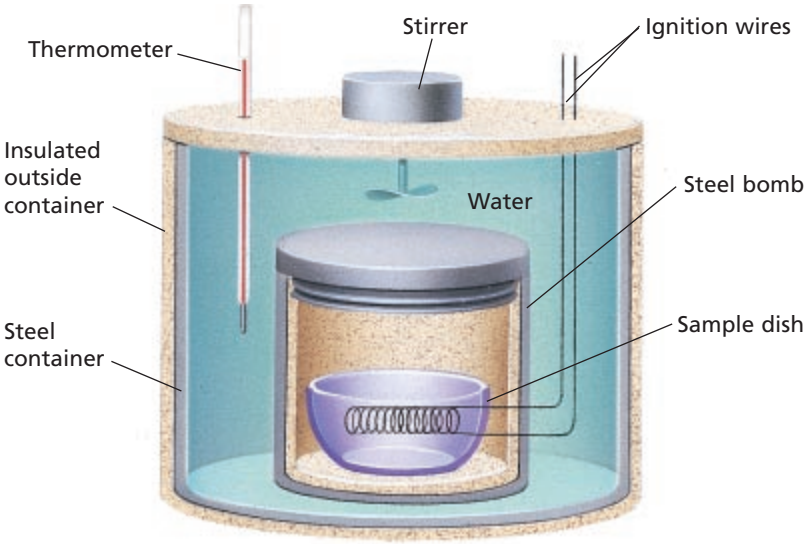

FIGURE 17-4 This is a diagram of a simple combustion calorimeter. A weighed sample is ignited by an electric spark and burned in the sample dish in an atmosphere of pure oxygen. The energy generated by the combustion reaction warms the steel bomb and the water surrounding it. The thermometer measures the initial and final temperatures of the water, and this temperature change is then used to calculate the energy evolved by the reaction as heat.

substance is called the **heat of combustion** *of the substance.* Heat of combustion is defined in terms of *one mole of reactant*, whereas the heat of formation is defined in terms of *one mole of product.* All substances are in their standard state. The general enthalpy notation, ΔH, applies to heats of reaction, but the addition of a subscripted *c*, ΔH_c, refers specifically to heat of combustion. A list of heats of combustion can be found in Appendix Table A-5 (page 896).

Carbon dioxide and water are the products of the complete combustion of organic compounds containing only carbon and hydrogen or carbon, hydrogen, and oxygen. Knowing this, we can write the thermochemical equation for the combustion of any organic compound listed by balancing the equation for the reaction of one mole of the compound. For example, propane is a major component of the fuel used for outdoor gas grills. Its reaction with oxygen in the air, forming carbon dioxide and water as products and releasing energy in the form of heat and light, is a common example of combustion. The complete combustion of one mole of propane, C_3H_8, is described by the following thermochemical equation.

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H_c^0 = -2219.2 \text{ kJ/mol}$$

Figure 17-4 shows a combustion calorimeter, one of the instruments used to determine heats of combustion.

Calculating Heats of Reaction

Thermochemical equations can be rearranged and added to give enthalpy changes for reactions not included in the data tables. The basis for calculating heats of reaction is known as **Hess's law:** *The overall enthalpy change in a reaction is equal to the sum of enthalpy changes for the individual steps in the process.* The energy difference between reactants and

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products is independent of the route taken to get from one to the other. In fact, measured heats of reaction can be combined to calculate heats of reaction that are difficult or impossible to actually measure.

To demonstrate how to apply Hess's law, we will work through the calculation of the heat of formation for the formation of methane gas, CH_4, from its elements, hydrogen gas and solid carbon (graphite), at 298.15 K (25°C).

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \quad \Delta H_f^0 = ?$$

In order to calculate the change in enthalpy for this reaction, we can use the combustion reactions of the elements, carbon and hydrogen, and of methane.

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H_c^0 = -393.5 \text{ kJ/mol}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_c^0 = -285.8 \text{ kJ/mol}$$
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^0 = -890.8 \text{ kJ/mol}$$

The general principles for combining thermochemical equations follow.

1. If a reaction is reversed, the sign of ΔH is also reversed.
2. Multiply the coefficients of the known equations so that when added together they give the desired thermochemical equation.

In this case, reverse the combustion equation for methane, and remember to change the sign of ΔH from negative to positive. This will change the exothermic reaction to an endothermic one.

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) \quad \Delta H^0 = +890.8 \text{ kJ/mol}$$

Now we notice that 2 formula units of water are used as a reactant; therefore, 2 formula units of water will be needed as a product. In the combustion reaction for hydrogen as it is written, it only produces one formula unit of water. We must multiply the coefficients of this combustion reaction and the value of ΔH by 2 in order to obtain the desired quantity of water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \quad \Delta H_c^0 = 2(-285.8 \text{ kJ/mol})$$

We are now ready to add the three equations together using Hess's law to give the heat of formation for methane and the balanced equation.

$$C(s) + \cancel{O_2(g)} \longrightarrow \cancel{CO_2(g)} \qquad \Delta H_c^0 = -393.5 \text{ kJ/mol}$$
$$2H_2(g) + \cancel{O_2(g)} \longrightarrow \cancel{2H_2O(l)} \qquad \Delta H_c^0 = 2(-285.8 \text{ kJ/mol})$$
$$\cancel{CO_2(g)} + \cancel{2H_2O(l)} \longrightarrow CH_4(g) + \cancel{2O_2(g)} \qquad \Delta H^0 = +890.8 \text{ kJ/mol}$$
$$\overline{C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H_f^0 = -74.3 \text{ kJ/mol}}$$

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SAMPLE PROBLEM 17-2

Calculate the heat of reaction for the combustion of nitrogen monoxide gas, NO, to form nitrogen dioxide gas, NO_2, as given in the following thermochemical equation.

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

Use the heat-of-formation data in Appendix Table A-14 (page 902). Solve by combining the known thermochemical equations. Verify the result by using the general equation for finding heats of reaction from heats of formation.

SOLUTION

1 ANALYZE

Given: $\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO(g)$ $\quad \Delta H_f^0 = +90.29$ kJ/mol

$\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)$ $\quad \Delta H_f^0 = +33.2$ kJ/mol

Unknown: ΔH^0 for $NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$

2 PLAN

The ΔH requested can be found by adding the ΔHs of the component reactions as specified in Hess's law. The desired equation has $NO(g)$ and $\tfrac{1}{2}O_2(g)$ as reactants and $NO_2(g)$ as the product.

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

We need an equation with NO as a reactant. Reversing the first reaction for the formation of NO from its elements and the sign of ΔH yields the following thermochemical equation.

$$NO(g) \longrightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^0 = -90.29 \text{ kJ/mol}$$

The other equation should have NO_2 as a product, so we can retain the second equation for the formation of NO_2 from its elements as it stands.

$$\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^0 = +33.2 \text{ kJ/mol}$$

3 COMPUTE

$$NO(g) \longrightarrow \cancel{\tfrac{1}{2}N_2(g)} + \cancel{\tfrac{1}{2}O_2(g)} \qquad \Delta H^0 = -90.29 \text{ kJ/mol}$$

$$\cancel{\tfrac{1}{2}N_2(g)} + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^0 = +33.2 \text{ kJ/mol}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g) \qquad \Delta H^0 = -57.1 \text{ kJ/mol}$$

Note the cancellation of the $\tfrac{1}{2}N_2(g)$ and the partial cancellation of the $O_2(g)$.

4 EVALUATE

The unnecessary reactants and products cancel to give the desired equation. The general relationship between the heat of a reaction and the heats of formation of the reactants and products is described in the following word equation.

$$\Delta H^0 = \text{sum of } \Delta H_f^0 \text{ of products} - \text{sum of } \Delta H_f^0 \text{ of reactants}$$

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To find the necessary sums, the ΔH_f^0 value for each reactant and each product must be multiplied by its respective coefficient in the desired equation. For the reaction of NO with O_2, applying this equation gives the following value for ΔH^0.

$$\Delta H^0 = \Delta H_f^0(NO_2) - [\Delta H_f^0(NO) + 0]$$
$$= +33.2 \text{ kJ/mol} - 90.29 \text{ kJ/mol} = -57.1 \text{ kJ/mol}$$

Note that zero is the assigned value for the heats of formation of elements in their standard states.

PRACTICE

1. Calculate the heat of reaction for the combustion of methane gas, CH_4, to form $CO_2(g) + H_2O(l)$.

Answer
–890.2 kJ/mol

2. Carbon occurs in two distinct forms. It can be the soft, black material found in pencils and lock lubricants, called graphite, or it can be the hard, brilliant gem we know as diamond. Calculate ΔH^0 for the conversion of graphite to diamond for the following reaction.

Answer
2 kJ/mol

$$C_{graphite}(s) \longrightarrow C_{diamond}(s)$$

The combustion reactions you will need follow.

$C_{graphite}(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H_c^0 = -394$ kJ/mol
$C_{diamond}(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H_c^0 = -396$ kJ/mol

Determining Heat of Formation

When carbon is burned in a limited supply of oxygen, carbon monoxide is produced. In this reaction, carbon is probably first oxidized to carbon dioxide. Then part of the carbon dioxide is reduced with carbon to give some carbon monoxide. Because these two reactions occur simultaneously and we get a mixture of CO and CO_2, it is not possible to directly measure the heat of formation of $CO(g)$ from $C(s)$ and $O_2(g)$.

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H_f^0 = ?$$

However, we do know the heat of formation of carbon dioxide and the heat of combustion of carbon monoxide.

$C(s) + O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H_f^0 = -393.5$ kJ/mol
$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $\quad \Delta H_c^0 = -283.0$ kJ/mol

We reverse the second equation because we need CO as a product. Adding gives the desired heat of formation of carbon monoxide.

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Heats of Reaction

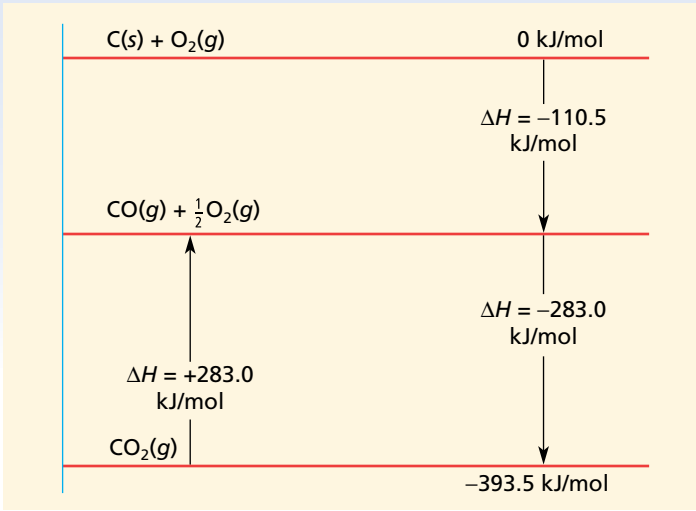

FIGURE 17-5 This diagram shows the heat of reaction for carbon dioxide, CO_2, and carbon monoxide, CO.

$$C(s) + O_2(g) \longrightarrow \cancel{CO_2(g)} \qquad \Delta H^0 = -393.5 \text{ kJ/mol}$$

$$\cancel{CO_2(g)} \longrightarrow CO(g) + \tfrac{1}{2}\cancel{O_2(g)} \qquad \Delta H^0 = +283.0 \text{ kJ/mol}$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H^0 = -110.5 \text{ kJ/mol}$$

Figure 17-5 is a model for the process described in this section. If we plot the reactions based on their relative energy, you can see the relationship among the values obtained for the heat of formation of carbon monoxide. The formation of CO_2 is plotted at a level corresponding to –393.5 kJ/mol. The diagram shows the reverse of the combustion reaction (+283.0 kJ/mol) is added to that level. From the diagram, you see the difference, which represents the formation of CO. This value is –110.5 kJ/mol.

SAMPLE PROBLEM 17-3

Calculate the heat of formation of pentane, C_5H_{12}, using the information on heats of formation in Appendix Table A-14 (page 902) and the information on heats of combustion in Appendix Table A-5 (page 896). Solve by combining the known thermochemical equations.

SOLUTION

1 *ANALYZE*

Given: $C(s) + O_2(g) \longrightarrow CO_2(g)$ $\qquad \Delta H_f^0 = -393.5$ kJ/mol

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\qquad \Delta H_f^0 = -285.8$ kJ/mol

$C_5H_{12}(g) + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(l)$ $\qquad \Delta H_c^0 = -3535.6$ kJ/mol

Unknown: ΔH_f^0 for $5C(s) + 6H_2(g) \longrightarrow C_5H_{12}(g)$

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2 PLAN

Combine the given equations according to Hess's law. We need C_5H_{12} as a product, so we reverse the equation for combustion of C_5H_{12} and the sign for ΔH_c^0. Multiply the equation for formation of CO_2 by 5 to give 5C as a reactant. Multiply the equation for formation of H_2O by 6 to give $6H_2$ as a reactant.

3 COMPUTE

$$5C(s) + \cancel{5O_2(g)} \longrightarrow \cancel{5CO_2(g)} \qquad \Delta H^0 = 5(-393.5 \text{ kJ/mol})$$

$$6H_2(g) + \cancel{3O_2(g)} \longrightarrow \cancel{6H_2O(l)} \qquad \Delta H^0 = 6(-285.8 \text{ kJ/mol})$$

$$\cancel{5CO_2(g)} + \cancel{6H_2O(l)} \longrightarrow C_5H_{12}(g) + \cancel{8O_2(g)} \qquad \Delta H^0 = +3535.6 \text{ kJ/mol}$$

$$5C(s) + 6H_2(g) \longrightarrow C_5H_{12}(g) \qquad \Delta H_f^0 = -145.7 \text{ kJ/mol}$$

4 EVALUATE

The unnecessary reactants and products cancel to give the correct equation.

PRACTICE

1. Calculate the heat of formation of butane, C_4H_{10}, using the balanced chemical equation and information in Appendix Table A-5 (page 896) and Table A-14 (page 902). Write out the solution according to Hess's law.

   Answer –125.4 kJ/mol

2. Calculate the heat of combustion of 1 mol of nitrogen, N_2, to form NO_2 using the balanced chemical equation and Appendix Table A-14 (page 902). (Hint: The heat of combustion of N_2 will be equal to the sum of the heats of formation of the combustion products of N_2 minus the heat of formation of N_2.)

   Answer + 66.4 kJ/mol

3. Calculate the heat of formation for sulfur dioxide, SO_2, from its elements, sulfur and oxygen. Use the balanced chemical equation and the following information.

   Answer –296.1 kJ/mol

$$S(s) + \tfrac{3}{2}O_2(g) \longrightarrow SO_3(g) \qquad \Delta H_c^0 = -395.2 \text{ kJ/mol}$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta H^0 = -198.2 \text{ kJ/mol}$$

SECTION REVIEW

1. What is meant by enthalpy change?
2. What is meant by heat of reaction?
3. Describe the relationship between a compound's stability and its heat of formation.
4. What is the importance of Hess's law to thermodynamic calculations?
5. How much energy would be absorbed as heat by 75 g of iron when heated from 295 K to 301 K?
6. When 1 mol of methane is burned at constant pressure, 890 kJ of energy is released as heat. If a 3.2 g sample of methane is burned at constant pressure, what will be the value of ΔH? (Hint: Convert the grams of methane to moles. Also make sure your answer has the correct sign for an exothermic process.)

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Self-Heating Meals

Who would have thought that corrosion could be useful? The HeaterMeals Company did. This company uses the properties of salt-water corrosion to heat TV-type dinners, and now it is taking packaged foods to a new level of convenience.

HeaterMeals' products, as their name implies, come with a self-contained heat source. Each meal contains a package of food, a tray that holds a porous pouch containing Mg and Fe alloy, and a 2 oz pouch filled with salt water. When the salt water is poured into the tray with the porous pouch, it begins to vigorously corrode the metals. The sealed, precooked food package is then placed on top of the tray and returned to its box, where the temperature of the food package is raised by 100°F, heating the meal in 14 min.

Corrosion, the process by which a metal reacts with air or water, is usually an undesirable event, such as when iron corrodes to form rust. With HeaterMeals, however, the corrosion process is speeded up to produce an exothermic reaction—with the excess heat as the desired result.

According to Drew McLandrich, of The HeaterMeals Company, the idea for using self-heating metallic alloy powders has been around since the 1930s. "But," says McLandrich, "there really have been no significant uses of the product until the Desert Storm conflict, which led to the military's taking this technology and adopting it for field use so that soldiers could heat a meal-ready-to-eat."

"We've made about 80 million heaters for the military in the last 10 years. Lately we've been successfully marketing them to long-distance truck drivers. The product is in about 800 truck stops in 48 states.

The company has plans to develop other products using the controlled use of "supercorrosion." "A beverage could be heated," says McLandrich, "and we do have prototypes for a baby-bottle warmer. We're also working on making a portable hot cup of coffee or a hot cup of tea or cocoa."

So the next time you need a hot meal and there are no kitchens or restaurants around, consider the possibilities of supercorrosion and exothermic reactions.

This product uses supercorrosion to give you a hot meal.

How did the development of self-heating metallic alloy powders benefit the military?

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SECTION 17-2

Objectives

- Explain the relationship between enthalpy change and the tendency of a reaction to occur.
- Explain the relationship between entropy change and the tendency of a reaction to occur.
- Discuss the concept of free energy, and explain how the value of this quantity is calculated and interpreted.
- Describe the use of free energy change to determine the tendency of a reaction to occur.

Driving Force of Reactions

The change in energy of a reaction system is one of two factors that allow chemists to predict whether a reaction will occur spontaneously and to explain how it occurs. The randomness of the particles in a system is the second factor affecting whether a reaction will occur spontaneously.

Enthalpy and Reaction Tendency

The great majority of chemical reactions in nature are exothermic. As these reactions proceed, energy is liberated and the products have less energy than the original reactants. The products are also more resistant to change, more stable, than the original reactants. The tendency throughout nature is for a reaction to proceed in a direction that leads to a lower energy state.

We might think that endothermic reactions, in which energy is absorbed, cannot occur spontaneously because the products are at higher potential energy and are less stable than the original reactants. They would be expected to proceed only with the assistance of an outside influence, such as continued heating. However, some endothermic reactions *do* occur spontaneously. We conclude that something other than enthalpy change must help determine whether a reaction will occur.

Entropy and Reaction Tendency

A naturally occurring endothermic process is melting. An ice cube melts spontaneously at room temperature as energy is transferred from the warm air to the ice. The well-ordered arrangement of water molecules in the ice crystal is lost, and the less-orderly liquid phase of higher energy content is formed. A system that can go from one state to another without an enthalpy change does so by becoming more disordered.

Look at the physical states of the reactants in the chemical equation for the decomposition of ammonium nitrate.

$$2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(l) + O_2(g)$$

CHEMISTRY INTERACTIVE TUTOR

Module 9: Thermochemistry

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On the left side are 2 mol of solid ammonium nitrate. The right-hand side of the equation shows 3 mol of gaseous molecules plus 4 mol of a liquid. The arrangement of particles on the right-hand side of the equation is more random than the arrangement on the left side of the equation and hence is less ordered. Figures 17-6(a) and (b) show the reactant and products of this decomposition reaction.

These examples illustrate that there is a tendency in nature to proceed in a direction that increases the disorder of a system. A disordered system is one that lacks a regular arrangement of its parts. This tendency toward disorder is called entropy. **Entropy,** *S,* can be defined in a simple qualitative way as *a measure of the degree of randomness of the particles, such as molecules, in a system*. In order to understand the concept of entropy, consider solids, liquids, and gases. In a solid, the particles are fixed in position in their small regions of space, but they are vibrating back and forth. Even so, we can determine with fair precision the location of the particles. The degree of randomness is low, so the entropy is low. When the solid melts, the particles are still very close together but they can move about somewhat. The system is more random, and it is more difficult to describe the location of the particles. The entropy is higher. When the liquid evaporates, the particles are moving rapidly and are also much farther apart. Locating an individual particle is much more difficult and the system is much more random. The entropy of the gas is still higher than that of the liquid. A general but not absolute rule is that the entropy of liquids is higher than that of solids, and the entropy of gases is higher than that of liquids. But this rule must be used with caution. For example, the entropy of liquid mercury is much lower than that of some solids.

(a)

(b)

FIGURE 17-6 When ammonium nitrate, NH_4NO_3, decomposes, the entropy of the reaction system increases as (a) one solid reactant becomes (b) two gaseous products and one liquid product.

At absolute zero, random motion ceases, so the entropy of a pure crystalline solid is by definition zero at absolute zero. As energy is added, the randomness of the molecular motion increases. Measurements of energy absorbed and calculations are used to determine the absolute entropy or standard molar entropy, and values are then recorded in tables. These molar values are reported as kJ/(mol•K). Entropy change, which can also be measured, is defined as the difference between the entropy of the products and the reactants. Therefore, an increase in entropy is represented by a positive value for ΔS, and a decrease in entropy is represented by a negative value for ΔS.

The process of forming a solution almost always involves an increase in entropy because there is an increase in randomness. This is true for mixing gases, dissolving a liquid in another liquid, and dissolving a solid in a liquid.

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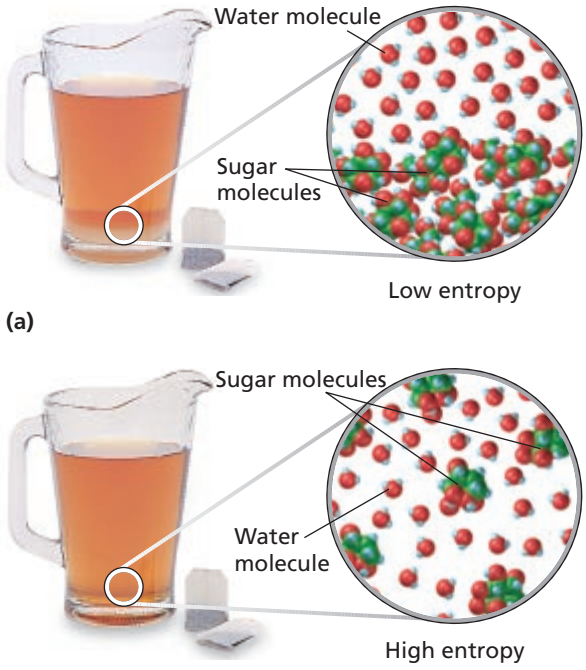

FIGURE 17-7 When a solid dissolves in a liquid, the entropy of the system increases.

Figure 17-7 illustrates the entropy change that takes place when solid sugar is dissolved in liquid tea. In the sugar-water system shown in Figure 17-7(a), the solid sugar has just been added to the tea, but most of it has not yet dissolved. The entropy is low because the majority of the sugar molecules are in one region at the bottom of the pitcher and the majority of the water molecules can be found everywhere else in the pitcher. After the sugar dissolves in the tea, shown in Figure 17-7(b), the sugar molecules are thoroughly mixed throughout the tea solution. Sugar molecules and water molecules might be found anywhere in the solution, so the entropy, the randomness, of the system increases. This would give ΔS a positive value for this solid-liquid system. You can imagine the same series of events happening for a system of gases mixing with each other or a system of liquids mixing. In each case, ΔS would have a positive value once the solution was formed.

Free Energy

Processes in nature are driven in two directions: toward lowest enthalpy and toward highest entropy. When these two oppose each other, the dominant factor determines the direction of change. To predict which factor will dominate for a given system, a function has been defined to relate the enthalpy and entropy factors at a given temperature. *This combined enthalpy-entropy function is called the* **free energy,** *G, of the system.* This function simultaneously assesses both the enthalpy-change and entropy-change tendencies. Natural processes proceed in the direction that lowers the free energy of a system.

Only the *change* in free energy can be measured. The change in free energy can be defined in terms of the changes in enthalpy and entropy. *At a constant pressure and temperature, the* **free-energy change,** ΔG*, of a system is defined as the difference between the change in enthalpy,* ΔH*, and the product of the Kelvin temperature and the entropy change, which is defined as* $T\Delta S$*.*

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Note that this expression is for substances in their standard states. The product $T\Delta S$ and the quantities ΔG and ΔH have the same units, usually kJ/mol. The units of ΔS for use in this equation are usually kJ/(mol•K).

Each of the variables in the free-energy equation can have positive or negative values. This leads to four possible combinations of terms.

Table 17-2 (page 529) shows us that if ΔH is negative and ΔS is positive, then both terms on the right in the free energy equation are negative. Both factors contribute to the process being spontaneous.

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Therefore, ΔG will always be negative, and the reaction is definitely spontaneous. On the other hand, if ΔH is positive (endothermic process) and ΔS is negative (decrease in randomness), then the reaction as written will definitely not occur. When the enthalpy and entropy changes are operating in different directions, sometimes one will predominate and sometimes the other will predominate. There are cases in which the enthalpy change is negative and the entropy change is negative. The enthalpy factor leads to a spontaneous process, but the negative entropy change opposes this. This is true in the following reaction. (The entropy decreases because there is a decrease in moles of gas.)

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

There is a fairly large decrease in entropy, $\Delta S^0 = -0.1207$ kJ/(mol•K). However, the reaction is strongly exothermic, with a $\Delta H^0 = -136.9$ kJ/mol. The reaction proceeds because the enthalpy term predominates.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -136.9 \text{ kJ/mol} - 298 \text{ K}[-0.1207 \text{ kJ/(mol•K)}]$$
$$= -101.1 \text{ kJ/mol}$$

We can contrast this with the common commercial process for the manufacture of syngas, a mixture of CO and H_2. (This gas mixture is the starting point for the synthesis of a number of large-volume commercial chemicals, such as methanol, CH_3OH.)

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

This reaction is endothermic, with $\Delta H^0 = +206.1$ kJ/mol and $\Delta S^0 = +0.215$ kJ/(mol•K), at standard conditions. The resulting ΔG is positive at room temperature. This tells us that the reaction will not occur at room temperature even though the entropy change is favorable.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = +206.1 \text{ kJ/mol} - 298 \text{ K}[+0.215 \text{ kJ/(mol•K)}]$$
$$= +142.0 \text{ kJ/mol}$$

TABLE 17-2 Relating Enthalpy, Entropy, and Free Energy Changes to Reaction Occurrence

ΔH	ΔS	ΔG
– value (exothermic)	+ value (disordering)	always negative
– value (exothermic)	– value (ordering)	negative at *lower* temperatures
+ value (endothermic)	+ value (disordering)	negative at *higher* temperatures
+ value (endothermic)	– value (ordering)	never negative

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SAMPLE PROBLEM 17-4

For the reaction $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$, at 298.15 K, ΔH^0 = 176 kJ/mol and ΔS^0 = 0.285 kJ/(mol•K). Calculate ΔG^0, and tell whether this reaction can proceed in the forward direction at 298.15 K.

SOLUTION

1 ANALYZE

Given: $\Delta H^0 = 176$ kJ/mol at 298.15 K
$\Delta S^0 = 0.285$ kJ/(mol•K) at 298.15 K
Unknown: ΔG^0 at 298.15 K

2 PLAN

$$\Delta S, \Delta H, T \rightarrow \Delta G$$

The value of ΔG can be calculated according to the following equation.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

3 COMPUTE

$$\begin{aligned}\Delta G^0 &= 176 \text{ kJ/mol} - 298 \text{ K } [0.285 \text{ kJ/(mol•K)}] \\ &= 176 \text{ kJ/mol} - 84.9 \text{ kJ/mol} \\ &= 91 \text{ kJ/mol}\end{aligned}$$

4 EVALUATE

The answer is reasonably close to an estimated value of 110, calculated as $200 - (300 \times 0.3)$. The positive value of ΔG shows that this reaction does not occur naturally at 298.15 K.

PRACTICE

1. For the vaporization reaction $Br_2(l) \longrightarrow Br_2(g)$, $\Delta H^0 = 31.0$ kJ/mol and $\Delta S^0 = 93.0$ J/(mol•K). At what temperature will this process be spontaneous?

Answer
above 333 K

SECTION REVIEW

1. What kind of enthalpy change favors a spontaneous reaction?
2. What is entropy, and how does it relate to spontaneity of reactions?
3. List several changes that result in an entropy increase.
4. Define *free energy*, and explain how its change is calculated.
5. Explain the relationship between free-energy change and spontaneity of reactions.
6. In the reaction in Sample Problem 17-4, why does the entropy increase?
7. How should increasing temperature affect the value of ΔG for the reaction in Sample Problem 17-4?
8. Predict the sign of ΔS^0 for each of the following reactions:
   a. the thermal decomposition of solid calcium carbonate
   $$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$
   b. the oxidation of SO_2 in air
   $$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

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The Reaction Process

SECTION 17-3

Objectives

- Explain the concept of reaction mechanism.
- Use the collision theory to interpret chemical reactions.
- Define *activated complex.*
- Relate activation energy to heat of reaction.

The enthalpy change, entropy change, and free energy of a chemical reaction are independent of the actual route by which a reaction occurs. What happens between the initial and final states of a reaction system is described by the energy pathway that a reaction follows and the changes that take place on the molecular level when substances interact.

Reaction Mechanisms

If you mix aqueous solutions of HCl and NaOH, an extremely rapid neutralization reaction occurs.

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l) + Na^+(aq) + Cl^-(aq)$$

The reaction is practically instantaneous; the rate is limited only by the speed with which the H_3O^+ and OH^- ions can diffuse through the water to meet each other. On the other hand, reactions between ions of the same charge and between molecular substances are not instantaneous. Negative ions repel each other, and the electron clouds of molecules repel each other strongly at very short distances. Therefore, only ions or molecules with very high kinetic energy can overcome repulsive forces and get close enough to react. In this section we will limit our discussion to reactions between molecules.

Colorless hydrogen gas consists of pairs of hydrogen atoms bonded together as diatomic molecules, H_2. Violet-colored iodine vapor is also diatomic, consisting of pairs of iodine atoms bonded together as I_2 molecules. A chemical reaction between these two gases at elevated temperatures produces hydrogen iodide, HI, a colorless gas. Hydrogen iodide molecules, in turn, tend to decompose and re-form hydrogen and iodine molecules, producing the violet gas shown in Figure 17-8. The following chemical equations describe these two reactions.

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$
$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

Such equations indicate only which molecular species disappear as a result of the reactions and which species are produced. They do not show the **reaction mechanism,** *the step-by-step sequence of reactions by which the overall chemical change occurs*.

FIGURE 17-8 Clear hydrogen iodide gas, HI, decomposes into clear hydrogen gas and violet iodine gas.

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Although only the net chemical change is directly observable for most chemical reactions, experiments can often be designed that suggest the probable sequence of steps in a reaction mechanism. Each reaction step is usually a simple process. The equation for each step represents the *actual* atoms, ions, or molecules that participate in that step. Even a reaction that appears from its balanced equation to be a simple process may actually be the result of several simple steps.

For many years, the formation of hydrogen iodide was considered a simple one-step process. It was thought to involve the interaction of two molecules, H_2 and I_2, in the forward reaction and two HI molecules in the reverse reaction. Experiments eventually showed, however, that a direct reaction between H_2 and I_2 does not take place.

Alternative mechanisms for the reaction were proposed based on the experimental results. The steps in each reaction mechanism had to add together to give the overall equation. Note that two of the species in the mechanism steps—I and H_2I—do not appear in the net equation. *Species that appear in some steps but not in the net equation are known as* **intermediates.** (Notice that they cancel each other out in the following mechanisms.) The first possible mechanism has the following two-step pathway.

Step 1: $I_2 \rightleftharpoons 2I$

Step 2: $2I + H_2 \rightleftharpoons 2HI$

$I_2 + H_2 \rightleftharpoons 2HI$

The second possible mechanism has a three-step pathway.

Step 1: $I_2 \rightleftharpoons 2I$

Step 2: $I + H_2 \rightleftharpoons H_2I$

Step 3: $H_2I + I \rightleftharpoons 2HI$

$I_2 + H_2 \rightleftharpoons 2HI$

The reaction between hydrogen gas and iodine vapor to produce hydrogen iodide gas is an example of a **homogeneous reaction,** *a reaction whose reactants and products exist in a single phase*—in this case, the gas phase. This reaction system is also an example of a homogeneous chemical system because all reactants and products in all intermediate steps are in the same phase.

Collision Theory

In order for reactions to occur between substances, their particles (molecules, atoms, or ions) must collide. Furthermore, these collisions must result in interactions. *The set of assumptions regarding collisions and reactions is known as* **collision theory.** Chemists use this theory to interpret many of their observations about chemical reactions.

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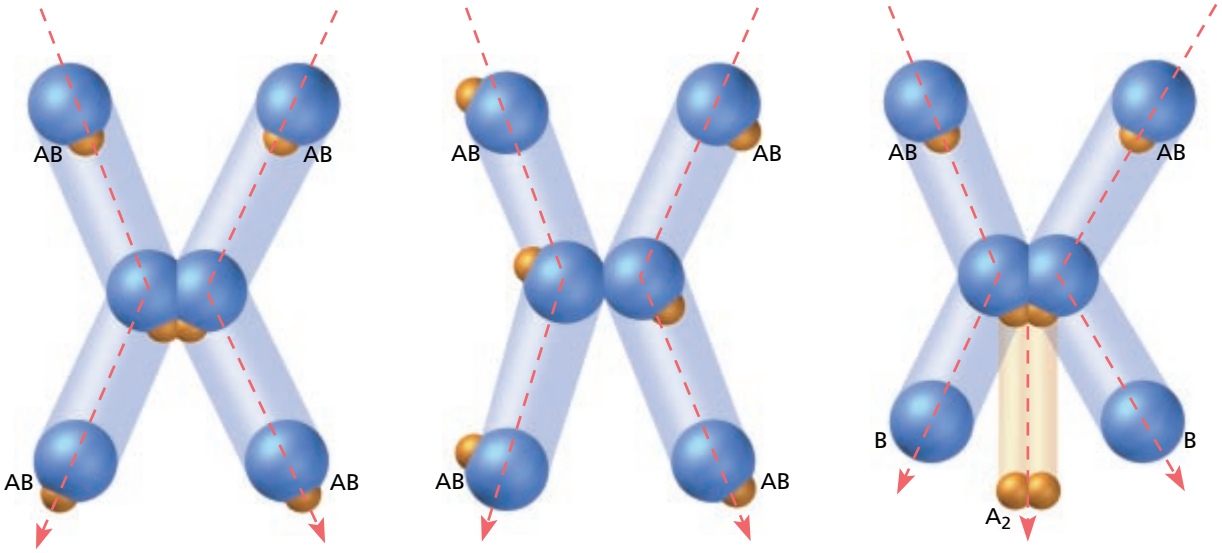

(a) Collision too gentle

(b) Collision in poor orientation

(c) Effective collision, correct orientation and energy

FIGURE 17-9 Three possible collision patterns for AB molecules are shown. Not every collision produces a chemical reaction.

Consider what might happen on a molecular scale in one step of a homogeneous reaction system. We will analyze a proposed first step in a hypothetical decomposition reaction.

$$AB + AB \rightleftharpoons A_2 + 2B$$

According to the collision theory, the two AB molecules must collide in order to react. Furthermore, they must collide while favorably oriented and with enough energy to merge the valence electrons and disrupt the bonds of the molecules. If they do so, a reshuffling of bonds leads to the formation of the products, one A_2 molecule and two B atoms. An effective collision is modeled in Figure 17-9(c).

If a collision is too gentle, the two molecules simply rebound from each other unchanged. This effect is illustrated in Figure 17-9(a). Similarly, a collision in which the reactant molecules are poorly oriented has little effect. The colliding molecules rebound without reacting. A poorly oriented collision is shown in Figure 17-9(b).

Thus, collision theory provides two reasons why a collision between reactant molecules may fail to produce a new chemical species: the collision is not energetic enough to supply the required energy, or the colliding molecules are not oriented in a way that enables them to react with each other.

Activation Energy

Consider the reaction for the formation of water from the diatomic gases oxygen and hydrogen according to the following equation.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

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Reaction Pathways for Forward and Reverse Reactions

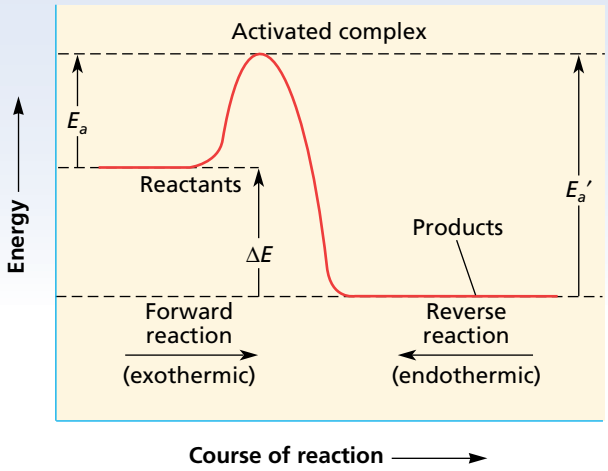

FIGURE 17-10 The difference between the activation energies for the reverse and forward reactions of a reversible reaction equals the energy change in the reaction, ΔE. The quantity for ΔE is the same for both directions, but is negative for the exothermic direction and positive for the endothermic direction.

The heat of formation is quite high: ΔH_f^0 = –285.8 kJ/mol at 298.15 K. The free-energy change is also large: ΔG^0 = –237.1 kJ/mol. Why, then, don't oxygen and hydrogen combine spontaneously and immediately to form water when they are mixed at room temperature?

Hydrogen and oxygen gases exist as diatomic molecules. When the molecules approach each other, the electron clouds repel each other and the molecules bounce off and never actually meet. In order for a reaction to occur, the colliding molecules must have enough kinetic energy to actually intermingle the valence electrons. In other words, the bonds of these molecular species must be broken in order for new bonds to be formed between oxygen and hydrogen atoms. Bond breaking is an endothermic process, and bond forming is exothermic. Even though the net process for forming water is exothermic, an initial input of energy is needed to overcome the repulsion forces that occur between reactant molecules when they are brought very close together. This initial energy input activates the reaction.

Once an exothermic reaction is started, the energy released is enough to sustain the reaction by activating other molecules. Thus, the reaction rate keeps increasing. It is limited only by the time required for reactant particles to acquire the energy and make contact. Energy from a flame or a spark, or the energy associated with high temperatures or radiations, may start exothermic reactants along the pathway of reaction. A generalized reaction pathway for an exothermic reaction is shown as the forward reaction in Figure 17-10. The minimum amount of energy needed to activate this reaction is the activation energy represented by E_a. **Activation energy** *is the minimum energy required to transform the reactants into an activated complex.*

The reverse reaction, decomposition of water molecules, is endothermic because the water molecules lie at an energy level that is lower than that of the hydrogen and oxygen molecules. The water molecules require a larger activation energy before they can decompose to reform oxygen and hydrogen. The energy needed to activate an endothermic reaction is greater than that required for the original exothermic change and is represented by E_a' in Figure 17-10. The difference between E_a' and E_a is equal to the energy change in the reaction, ΔE. This energy change has the same numerical value for the forward reaction as it has for the reverse reaction but with the opposite sign.

The Activated Complex

When molecules collide, some of their high kinetic energy is converted into internal potential energy within the colliding molecules. If enough

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energy is converted, molecules with suitable orientation become activated. New bonds can then form. In this brief interval of bond breakage and bond formation, the collision complex is in a transition state. Some sort of partial bonding exists in this transitional structure. *A transitional structure that results from an effective collision and that persists while old bonds are breaking and new bonds are forming is called an* **activated complex.** The exact structure of this activated complex is not known.

Figure 17-11 graphically breaks down the reaction pathway of the formation of hydrogen iodide gas described on page 532 into three steps. Beginning with the reactants, H_2 and I_2, we see that a certain amount of activation energy, E_{a1}, is needed to form the activated complex that leads to the formation of the intermediates H_2 and 2I. During the course of the reaction, more activation energy, E_{a2}, is needed to form the activated complex leading to the intermediates H_2I and I. In order to arrive at the final product, 2HI, another increase in activation energy is necessary, as seen by the highest peak labeled E_{a3}.

An activated complex is formed when an effective collision raises the internal energies of the reactants to their minimum level for reaction, as shown in Figure 17-10. Both forward and reverse reactions go through the same activated complex. A bond that is broken in the activated complex for the forward reaction must be re-formed in the activated complex for the reverse reaction. Observe that an activated complex occurs at a high-energy position along the reaction pathway. In this sense, the activated complex defines the activation energy for the system.

From the kinetic-molecular theory presented in Chapter 10, you know that the speeds and therefore the kinetic energies of the molecules increase as the temperature increases. An increase in speed causes more collisions, which can cause an increase in reactions. However, the increase in reactions depends on more than simply the number of collisions, as Figure 17-9 illustrates. The collisions between molecules must possess sufficient energy to form an activated complex or a reaction will not take place. Raising the temperature of a reaction provides more molecules with this activation energy, causing an increase in reactions.

In its brief existence, the activated complex has partial bonding that is characteristic of both reactant and product. In this state, it may re-form the original bonds and separate back into the reactant particles, or it may form new bonds and separate into product particles. Usually, the formation of products is just as likely as the formation of reactants. Do not confuse the activated complex with the relatively stable intermediate products of different steps of a reaction mechanism. The activated complex, unlike intermediate products, is a very short-lived molecular complex in which bonds are in the process of being broken and formed.

Activation Energy Peaks in the Formation of Activated Complexes

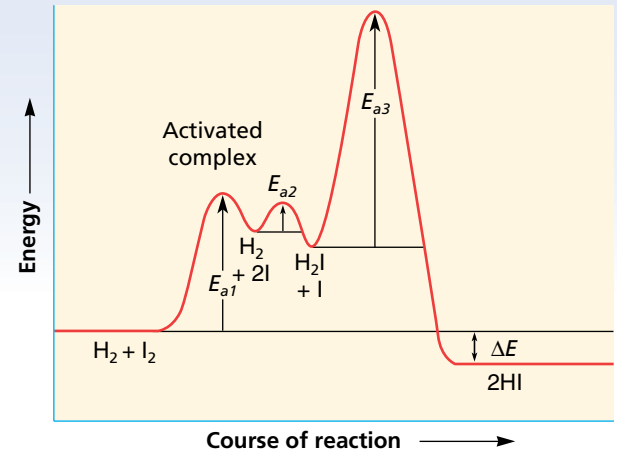

FIGURE 17-11 This energy profile graphically shows the formation of activated complexes during the gas-phase reaction $H_2 + I_2 \longrightarrow 2HI$.

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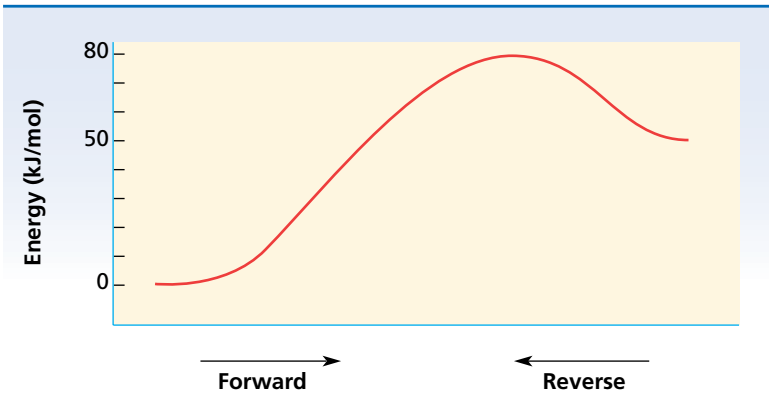
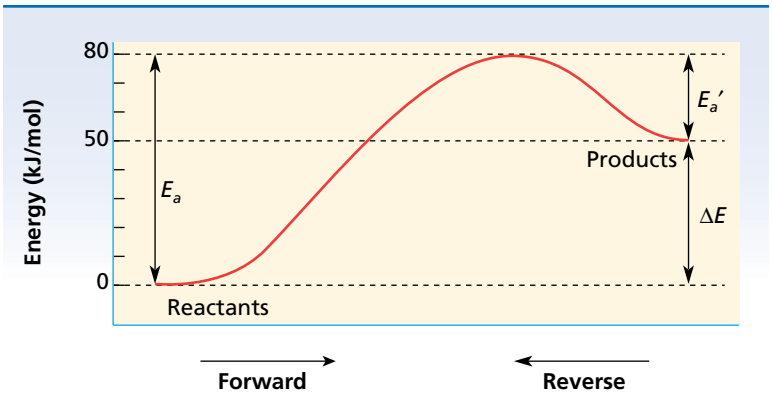
SAMPLE PROBLEM 17-5

Copy the energy diagram below, and label the reactants, products, ΔE, E_a, *and* E_a'. Determine the value of $\Delta E_{forward}$, $\Delta E_{reverse}$, E_a, and E_a'.



SOLUTION

The energy level of reactants is always at the left-hand end of such a curve, and the energy level of products is always at the right-hand end. The energy change in the reaction, ΔE, is the difference between these two energy levels. The activation energy differs in the forward and reverse directions. As E_a, it is the difference between the reactant energy level and the peak in the curve. As E_a', it is the difference between the product energy level and the peak in the curve. It is the minimum energy needed to achieve effective reaction in either direction.



$\Delta E_{forward}$ = energy of products – energy of reactants
$\Delta E_{forward}$ = 50 kJ/mol – 0 kJ/mol = +50 kJ/mol

$\Delta E_{reverse}$ = energy of reactants – energy of products
$\Delta E_{reverse}$ = 0 kJ/mol – 50 kJ/mol = – 50 kJ/mol

E_a = energy of activated complex – energy of reactants
E_a = 80 kJ/mol – 0 kJ/mol = 80 kJ/mol

E_a' = energy of activated complex – energy of products
E_a' = 80 kJ/mol – 50 kJ/mol = 30 kJ/mol

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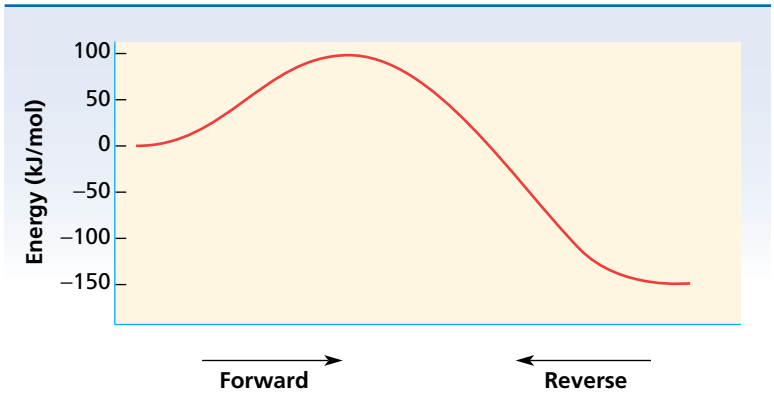
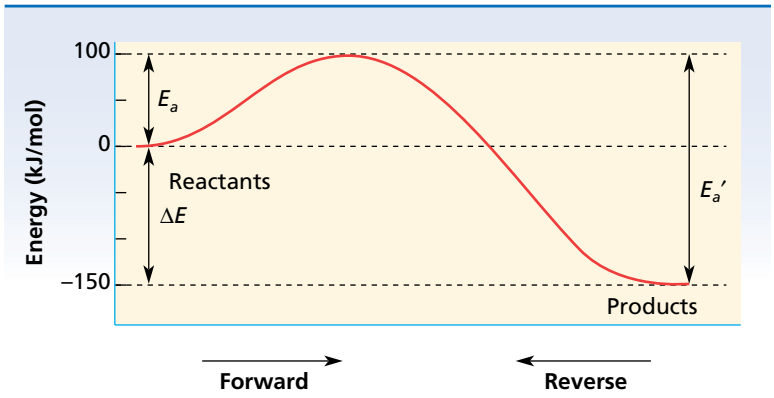
PRACTICE

1. Use the method shown in the sample problem to redraw and label the following energy diagram. Determine the value of $\Delta E_{forward}$, $\Delta E_{reverse}$, E_a, and E_a'.



Answer



$\Delta E_{forward} = -150$ kJ/mol
$\Delta E_{reverse} = +150$ kJ/mol

$E_a = 100$ kJ/mol
$E_a' = 250$ kJ/mol

SECTION REVIEW

1. What is meant by reaction mechanism?
2. What factors determine whether a molecular collision produces a reaction?
3. What is activation energy?
4. What is an activated complex?
5. How is activation energy related to the energy of reaction?

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SECTION 17-4

Reaction Rate

Objectives

- Define *chemical kinetics*, and explain the two conditions necessary for chemical reactions to occur.
- Discuss the five factors that influence reaction rate.
- Define *catalyst*, and discuss two different types.
- Explain and write rate laws for chemical reactions.

The change in concentration of reactants per unit time as a reaction proceeds is called the **reaction rate.** The study of reaction rates is concerned with the factors that affect the rate and with the mathematical expressions that reveal the specific dependencies of the rate on concentration. *The area of chemistry that is concerned with reaction rates and reaction mechanisms is called* **chemical kinetics.**

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Rate-Influencing Factors

For reactions other than simple decompositions to occur, particles must come into contact in a favorable orientation and with enough energy for activation. Thus, the rate of a reaction depends on the collision frequency of the reactants and on the collision efficiency. Any change in reaction conditions that affects the collision frequency, the collision efficiency, or the collision energy affects the reaction rate. Five important factors influence the rate of a chemical reaction.

Nature of Reactants

Substances vary greatly in their tendencies to react. For example, hydrogen combines vigorously with chlorine under certain conditions. Under the same conditions, it may react only feebly with nitrogen. Sodium and oxygen combine much more rapidly than iron and oxygen under similar conditions. Bonds are broken and other bonds are formed in reactions. The rate of reaction depends on the particular reactants and bonds involved.

Surface Area

Gaseous mixtures and dissolved particles can mix and collide freely; therefore, reactions involving them can occur rapidly. In heterogeneous reactions, the reaction rate depends on the area of contact of the reaction substances. **Heterogeneous reactions** *involve reactants in two different phases.* These reactions can occur only when the two phases are in contact. Thus, the surface area of a solid reactant is an important factor in determining rate. An increase in surface area increases the rate of heterogeneous reactions.

Solid zinc reacts with aqueous hydrochloric acid to produce zinc chloride and hydrogen gas according to the following equation.

$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$$

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This reaction occurs at the surface of the zinc solid. A cube of zinc measuring 1 cm on each edge presents only 6 cm^2 of contact area. The same amount of zinc in the form of a fine powder might provide a contact area thousands of times greater than the original area. Consequently, the reaction rate of the powdered solid is much higher.

A lump of coal burns slowly when kindled in air. The rate of burning can be increased by breaking the lump into smaller pieces, exposing more surface area. If the piece of coal is powdered and then ignited while suspended in air, it burns explosively. This is the cause of some explosions in coal mines.

Temperature

An increase in temperature increases the average kinetic energy of the particles in a substance; this can result in a greater number of effective collisions when the substance is allowed to react with another substance. If the number of effective collisions increases, the reaction rate will increase.

To be effective, the energy of the collisions must be equal to or greater than the activation energy. At higher temperatures, more particles possess enough energy to form the activated complex when collisions occur. Thus, a rise in temperature produces an increase in collision energy as well as in collision frequency.

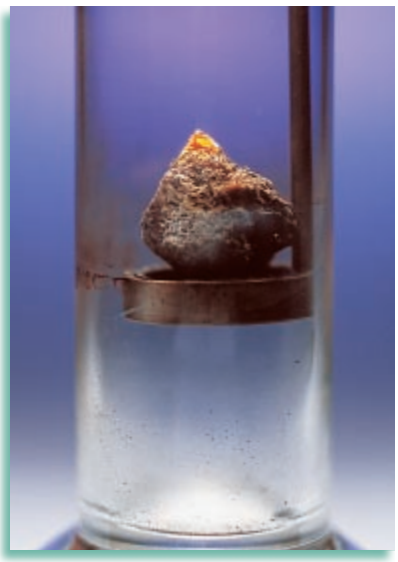
Decreasing the temperature of a reaction system has the opposite effect. The average kinetic energy of the particles decreases, so they collide less frequently and with less energy, producing fewer effective collisions. Beginning near room temperature, the reaction rates of many common reactions roughly double with each 10 K (10°C) rise in temperature. This rule of thumb should be used with caution, however. The actual rate increase with a given rise in temperature must be determined experimentally.

Concentration

Pure oxygen has five times the concentration of oxygen molecules that air has at the same pressure; consequently, a substance that oxidizes in air oxidizes more vigorously in pure oxygen. For example, in Figure 17-12, the light produced when the lump of charcoal is burned in pure oxygen is much more intense than the light produced when the charcoal lump is heated in air until combustion begins. The oxidation of charcoal is a heterogeneous reaction system in which one reactant is a gas. The reaction rate depends not only on the amount of exposed charcoal surface but also on the concentration of the reacting species, O_2.

In homogeneous reaction systems, reaction rates depend on the concentration of the reactants. Predicting the mathematical relationship between rate and concentration is difficult because most chemical reactions occur in a series of steps, and only one of these steps determines the reaction rate. If the number of effective collisions increases, the rate

(a)



(b)

FIGURE 17-12 Carbon burns faster in pure oxygen (a) than in air (b) because the concentration of the reacting species, O_2, is greater.

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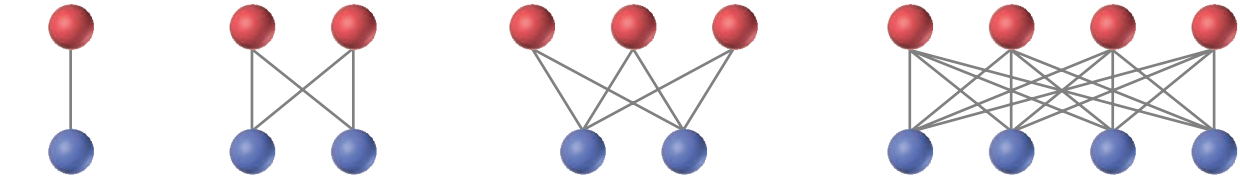

FIGURE 17-13 The concentration of reacting species affects the number of collisions and therefore the reaction rate.

increases as well. In general, an increase in rate is expected if the concentration of one or more of the reactants is increased, as depicted by the model in Figure 17-13. In the system with only two molecules, shown in Figure 17-13(a), only one collision can possibly occur. When there are four molecules in the system, as in Figure 17-13(b), there can be four possible collisions. Under constant conditions, as the number of molecules in the system increases, so does the total number of possible collisions between them. Figure 17-13(c) and (d) show a five- and eight-molecule system, allowing six and sixteen possible collisions, respectively. Lowering the concentration should have the opposite effect. The actual effect of concentration changes on reaction rate, however, must be determined experimentally.

FIGURE 17-14 The reaction rate of the decomposition of hydrogen peroxide, H_2O_2, can be increased by using a catalyst. The catalyst used here is manganese dioxide, MnO_2, a black solid. A 30% H_2O_2 solution is added dropwise onto the MnO_2 in the beaker and rapidly decomposes to O_2 and H_2O. Both the oxygen and water appear as gases because the high heat of reaction causes the water to vaporize.

Presence of Catalysts

Some chemical reactions proceed quite slowly. Sometimes their reaction rates can be increased dramatically by the presence of a catalyst. *A* **catalyst** *is a substance that changes the rate of a chemical reaction without itself being permanently consumed. The action of a catalyst is called* **catalysis.** The catalysis of the decomposition reaction of hydrogen peroxide by manganese dioxide is shown in Figure 17-14. A catalyst provides an alternative energy pathway or reaction mechanism in which the potential-energy barrier between reactants and products is lowered. The catalyst may be effective in forming an alternative activated complex that requires a lower activation energy—as suggested in the energy profiles of the decomposition of hydrogen peroxide, H_2O_2, shown in Figure 17-15—according to the following equation.

$$2H_2O_2(l) \longrightarrow O_2(g) + 2H_2O(l)$$

Catalysts do not appear among the final products of reactions they accelerate. They may participate in one step along a reaction pathway and be regenerated in a later step. In large-scale and cost-sensitive reaction systems, catalysts are recovered and reused. *A catalyst that is in the same phase as all the reactants and products in a reaction system is called a* **homogeneous catalyst.** *When its phase is different from that of the reactants, it is called a* **heterogeneous catalyst.** Metals are often used as heterogeneous catalysts. The catalysis of many reactions is promoted by adsorption of reactants on the metal surfaces, which has the effect of increasing the concentration of the reactants.

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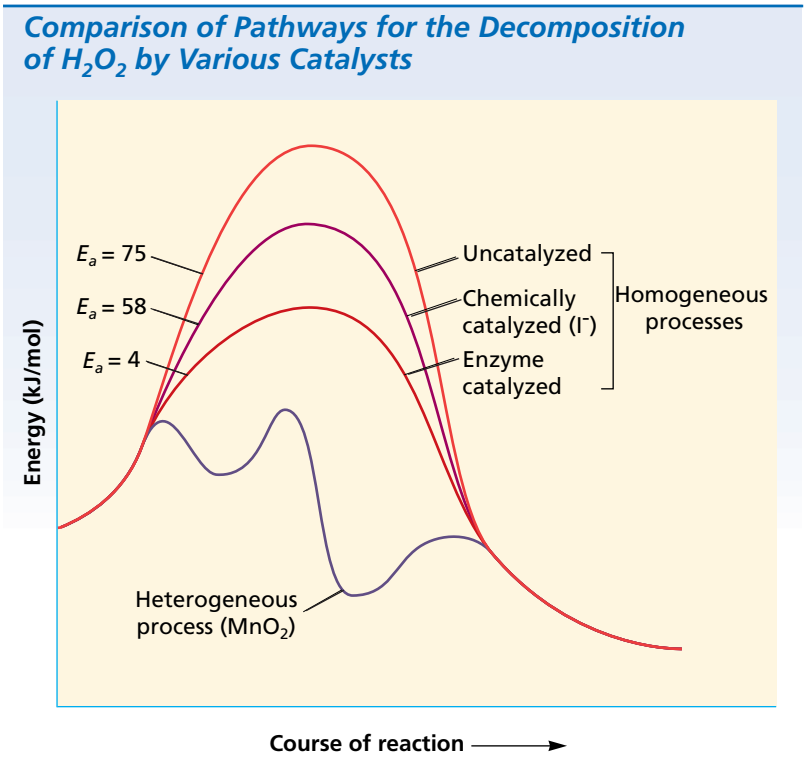

FIGURE 17-15 The activation energy for a chemical reaction can be reduced by adding an appropriate catalyst.

Rate Laws for Reactions

The relationship between the rate of a reaction and the concentration of one reactant is determined experimentally by first keeping the concentrations of other reactants and the temperature of the system constant. Then the reaction rate is measured for various concentrations of the reactant in question. A series of such experiments reveals how the concentration of each reactant affects the reaction rate.

Hydrogen gas reacts with nitrogen monoxide gas at constant volume and at an elevated constant temperature, according to the following equation.

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

Four moles of reactant gases produce three moles of product gases; thus, the pressure of the system diminishes as the reaction proceeds. The rate of the reaction can, therefore, be determined by measuring the change of pressure in the vessel with time.

Suppose a series of experiments is conducted using the same initial concentration of nitrogen monoxide but different initial concentrations of hydrogen. The initial reaction rate is found to vary directly with the hydrogen concentration: doubling the concentration of H_2 doubles the rate, and tripling the concentration of H_2 triples the rate. If R represents the reaction rate and $[H_2]$ is the concentration of hydrogen in moles per

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liter, the mathematical relationship between rate and concentration can be expressed as follows.

$$R \propto [H_2]$$

The $\propto$ is a symbol that is read "is proportional to."

Now suppose the same initial concentration of hydrogen is used but the initial concentration of nitrogen monoxide is varied. The initial reaction rate is found to increase fourfold when the NO concentration is doubled and ninefold when the concentration of NO is tripled. Thus, the reaction rate varies directly with the square of the nitrogen monoxide concentration, as described by the following proportion.

$$R \propto [NO]^2$$

Because R is proportional to $[H_2]$ and to $[NO]^2$, it is proportional to their product.

$$R \propto [H_2][NO]^2$$

By introduction of an appropriate proportionality constant, k, the expression becomes an equality.

$$R = k[H_2][NO]^2$$

An equation that relates reaction rate and concentrations of reactants is called the **rate law** *for the reaction.* It is applicable for a specific reaction at a given temperature. A rise in temperature increases the reaction rates of most reactions. The value of k usually increases as the temperature increases, but the relationship between reaction rate and concentration almost always remains unchanged.

Rate Laws and Reaction Pathway

The form of the rate law depends on the reaction mechanism. For a reaction that occurs in a *single step,* the reaction rate of that step is proportional to the product of the reactant concentrations, each of which is raised to its stoichiometric coefficient. For example, suppose one molecule of gas A collides with one molecule of gas B to form two molecules of substance C, according to the following equation.

$$A + B \longrightarrow 2C$$

One particle of each reactant is involved in each collision. Thus, doubling the concentration of either reactant will double the collision frequency. It will also double the reaction rate *for this step.* Therefore, the rate for this step is directly proportional to the concentration of A and B. The rate law for this one-step reaction follows.

$$R = k[A][B]$$

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Now suppose the reaction is reversible. In the reverse step, two molecules of C must decompose to form one molecule of A and one of B.

$$2C \longrightarrow A + B$$

Thus, the reaction rate for this reverse step is directly proportional to [C] × [C]. The rate law for the step is as follows.

$$R = k[C]^2$$

The power to which the molar concentration of each reactant is raised in the rate laws above corresponds to the coefficient for the reactant in the balanced chemical equation. Such a relationship holds *only* if the reaction follows a simple one-step path, that is, if the reaction occurs at the molecular level exactly as written in the chemical equation.

If a chemical reaction proceeds in a sequence of steps, the rate law is determined from the slowest step because it has the lowest rate. *This slowest-rate step is called the* **rate-determining step** *for the chemical reaction*.

Consider the reaction of nitrogen dioxide and carbon monoxide.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

The reaction is believed to be a two-step process represented by the following mechanism.

Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ slow
Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ fast

In the first step, two molecules of NO_2 collide, forming the intermediate species NO_3. This structure then collides with one molecule of CO and reacts quickly to produce one molecule each of NO_2 and CO_2. The first step is the slower of the two and is therefore the rate-determining step. We can write the rate law from this rate-determining step.

$$R = k[NO_2]^2$$

This tells us that two molecules of NO_2 are the reactants in the slower, rate-determining step. CO does not appear in the rate law because it reacts after the rate-determining step, so the reaction rate will not depend on [CO].

The general form for the rate law is given by the following equation.

$$R = k[A]^n[B]^m \ldots$$

The reaction rate is represented by R, k is the rate constant, and [A] and [B]. . . represent the molar concentrations of reactants. The n and m are the respective powers to which the concentrations are raised. They must be determined from *experimental data*.

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SAMPLE PROBLEM 17-6

Nitrogen dioxide and fluorine react in the gas phase according to the following equation.

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

A proposed mechanism for this reaction follows.

Step 1: $NO_2 + F_2 \longrightarrow NO_2F + F$ **slow**
Step 2: $F + NO_2 \longrightarrow NO_2F$ **fast**

Identify the rate-determining step and write an acceptable rate law.

SOLUTION

If we combine these two steps, the intermediate, F, cancels out and we are left with the original equation. The first step is the slower step, and is considered the rate-determining step. We can write the rate law from this rate-determining step.

$$R = k\,[NO_2][F_2]$$

SAMPLE PROBLEM 17-7

A reaction involving reactants X and Y was found to occur by a one-step mechanism: $X + 2Y \longrightarrow XY_2$. Write the rate law for this reaction, and then determine the effect of each of the following on the reaction rate:
a. doubling the concentration of X
b. doubling the concentration of Y
c. using one-third the concentration of Y

SOLUTION

Because the equation represents a single-step mechanism, the rate law can be written from the equation (otherwise, it could not be). The rate will vary directly with the concentration of X, which has an implied coefficient of 1 in the equation, and will vary directly with the square of the concentration of Y, which has the coefficient of 2: $R = k[X][Y]^2$.

a. Doubling the concentration of X will double the rate ($R = k[2X][Y]^2$).
b. Doubling the concentration of Y will increase the rate fourfold ($R = k[X][2Y]^2$).
c. Using one-third the concentration of Y will reduce the rate to one-ninth of its original value ($R = k[X][\frac{1}{3}Y]^2$).

PRACTICE

1. The rate of a reaction involving L, M, and N is found to double if the concentration of L is doubled, to increase eightfold if the concentration of M is doubled, and to double if the concentration of N is doubled. Write the rate law for this reaction.

   Answer
   $R = k[L][M]^3[N]$

2. At temperatures below 498 K, the following reaction takes place.

   $$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

   Doubling the concentration of NO_2 quadruples the rate of CO_2 being formed if the CO concentration is held constant. However, doubling the concentration of CO has no effect on the rate of CO_2 formation. Write a rate-law expression for this reaction.

   Answer
   $R = k[NO_2]^2$

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Quick LAB

Factors Influencing Reaction Rate

Wear Safety Goggles and an Apron.

Materials

- Bunsen burner
- paper ash
- copper foil strip
- graduated cylinder, 10 mL
- magnesium ribbon
- matches
- paper clip
- sandpaper
- steel wool
- 2 sugar cubes
- white vinegar
- zinc strip
- 6 test tubes, 16 × 150 mm
- tongs

Question

How do the type of reactants, surface area of reactants, concentration of reactants, and catalysts affect the rates of chemical reactions?

Procedure

Remove all combustible material from the work area. Wear safety goggles and an apron. Record all your results in a data table.

1. Add 10 mL of vinegar to each of three test tubes. To one test tube, add a 3 cm piece of magnesium ribbon; to a second, add a 3 cm zinc strip; and to a third, add a 3 cm copper strip. (All metals should be the same width.) If necessary, sandpaper the metals until they are shiny.
2. Using tongs, hold a paper clip in the hottest part of the burner flame for 30 s. Repeat with a ball of steel wool 2 cm in diameter.
3. To one test tube, add 10 mL of vinegar; to a second, add 5 mL of vinegar plus 5 mL of water; and to a third, add 2.5 mL of vinegar plus 7.5 mL of water. To each of the three test tubes, add a 3 cm piece of magnesium ribbon.
4. Using tongs, hold a sugar cube and try to ignite it with a match. Then try to ignite it in a burner flame. Rub paper ash on a second cube, and try to ignite it with a match.

Discussion

1. What are the rate-influencing factors in each step of the procedure?
2. What were the results from each step of the procedure? How do you interpret each result?

SECTION REVIEW

1. What is studied in the branch of chemistry that is known as chemical kinetics?
2. List the five important factors that influence the rate of chemical reactions.
3. What is a catalyst? Explain the effect of a catalyst on the rate of chemical reactions. How does a catalyst influence the activation energy required by a particular reaction?
4. What is meant by a rate law for a chemical reaction? Explain the conditions under which a rate law can be written from a chemical equation. When can a rate law not be written from a single step?

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CHAPTER 17 REVIEW

CHAPTER SUMMARY

17-1

- Thermochemistry is the study of the changes in energy that accompany chemical reactions and physical changes.
- A thermochemical equation is an equation that includes the quantity of energy released or absorbed as heat during the reaction as written.
- The heat of reaction is the quantity of energy released or absorbed as heat during a chemical reaction.
- An enthalpy change is the amount of energy absorbed or lost as heat by a system in a process carried out at constant pressure.
- The heat of reaction is negative for exothermic reactions and positive for endothermic reactions.
- Compounds with highly negative heats of formation tend to be stable; compounds with highly positive or only slightly negative heats of formation tend to be unstable.
- The standard molar heat of formation is the energy absorbed or released as heat in the formation of one mole of a compound from its elements in their standard states at 25°C.
- The energy released as heat in a combustion reaction is called the heat of combustion.
- Heats of reaction can be calculated by using heats of formation of reactants and products.

Vocabulary

calorimeter (511)
enthalpy change (516)
heat (512)
heat of combustion (519)
heat of reaction (514)
Hess's law (519)
joule (511)
molar heat of formation (517)
specific heat (512)
temperature (511)
thermochemical equation (515)
thermochemistry (511)

17-2

- The tendency throughout nature is for a reaction to proceed in the direction that leads to a lower energy state.
- Entropy is a measure of the disorder of a system.
- Free-energy change combines the effects of entropy and enthalpy changes and temperature of a system, and it is a measure of the overall tendency toward natural change.
- A reaction can occur spontaneously if it is accompanied by a decrease in free energy. It cannot occur spontaneously if there is an increase in free energy.

Vocabulary

entropy (527)
free energy (528)
free-energy change (528)

17-3

- The step-by-step process by which an overall chemical reaction occurs is called the reaction mechanism.
- In order for chemical reactions to occur, the particles of the reactants must collide.
- Activation energy is needed to merge valence electrons and loosen bonds sufficiently for molecules to react.
- An activated complex is formed when an effective collision between molecules of reactants raises the internal energy to the minimum level necessary for a reaction to occur.

Vocabulary

activated complex (535)
activation energy (534)
collision theory (532)
homogeneous reaction (532)
intermediates (532)
reaction mechanism (531)

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CHAPTER SUMMARY (continued)

17-4

- The rate of reaction is influenced by the following factors: nature of reactants, surface area, temperature, concentration of reactants, and the presence of catalysts and inhibitors.
- The rates at which chemical reactions occur can sometimes be experimentally measured and expressed in terms of mathematical equations called rate laws.

Vocabulary

catalysis (540)
catalyst (540)
chemical kinetics (538)
heterogeneous catalyst (540)
heterogeneous reactions (538)
homogeneous catalyst (540)
rate-determining step (543)
rate law (542)
reaction rate (538)

REVIEWING CONCEPTS

1. How does the energy of the products of a reaction system compare with the energy of the reactants when the reaction is
a. endothermic?
b. exothermic? (17-1)

2. a. Distinguish between heats of reaction, formation, and combustion.
b. On what basis are heats of formation and combustion defined? (17-1)

3. Write the equation that can be used to calculate the heat of reaction from heats of formation. (17-1)

4. What factors affect the value of ΔH in a reaction system? (17-1)

5. Would entropy increase or decrease for phase changes in which the reactant is a gas or liquid and the product is a solid? What sign would the entropy change have? (17-2)

6. How does an increase in temperature affect the entropy of a system? (17-2)

7. What combination of ΔH and ΔS values always produces a negative free-energy change? (17-2)

8. Explain the relationship between temperature and the tendency for reactions to occur spontaneously. (17-2)

9. a. What is the collision theory?
b. According to this theory, what two conditions must be met in order for a collision between reactant molecules to be effective in producing new chemical species? (17-3)

10. a. What condition must be met in order for an activated complex to result from the collision of reactant particles?
b. Where, in terms of energy, does the activated complex occur along a typical reaction pathway? (17-3)

11. In a reversible reaction, how does the activation energy required for the exothermic change compare with the activation energy required for the endothermic change? (17-3)

12. Would you expect the following equation to represent the mechanism by which ethane (C_2H_6) burns? Why or why not? (17-3)

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$

13. The decomposition of nitrogen dioxide $2NO_2 \longrightarrow 2NO + O_2$ occurs in a two-step sequence at elevated temperatures. The first step is $NO_2 \longrightarrow NO + O$. Predict a possible second step that, when combined with the first step, gives the complete reaction. (17-3)

14. What is meant by the rate-determining step for a chemical reaction? (17-4)

15. Write the general equation for the rate law, and label the various factors. (17-4)

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PROBLEMS

Specific Heat

16. How much heat energy is needed to raise the temperature of a 55 g sample of aluminum from 22.4°C to 94.6°C? Refer to Table 17-1 for the specific heat of aluminum. (Hint: See Sample Problem 17-1.)

17. 3.5 kJ of heat are added to a 28.2 g sample of iron at 20°C. What is the final temperature of the iron in kelvins? Refer to Table 17-1 for the specific heat of iron.

Reaction Heat

18. For each equation listed below, determine the ΔH and type of reaction (endothermic or exothermic).

a. $C(s) + O_2(g) \longrightarrow CO_2(g) + 393.51\ kJ$

b. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) + 890.31\ kJ$

c. $CaCO_3(s) + 176\ kJ \longrightarrow CaO(s) + CO_2(g)$

d. $H_2O(g) \longrightarrow H_2O(l) + 44.02\ kJ$

19. Rewrite each equation below with the ΔH value included with either the reactants or the products, and identify the reaction as endothermic or exothermic.

a. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H^0 = -285.83\ kJ/mol$

b. $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$; $\Delta H^0 = -1200\ kJ/mol$

c. $I_2(s) \longrightarrow I_2(g)$; $\Delta H^0 = +62.4\ kJ/mol$

d. $3CO(g) + Fe_2O_3(s) \longrightarrow 2Fe(s) + 3CO_2(g)$; $\Delta H^0 = -24.7\ kJ/mol$

20. Use Appendix Table A-14 to write the reaction illustrating the formation of each of the following compounds from its elements. Write the ΔH as part of each equation, and indicate the ΔH for the reverse reaction.

a. $CaCl_2(s)$

b. $C_2H_2(g)$ (ethyne or acetylene)

c. $SO_2(g)$

21. Use heat-of-formation data given in Appendix Table A-14 (page 902) to calculate the heat of reaction for each of the following. Solve each by combining the known thermochemical equations. Verify each result by using the general equation for finding heats of reaction from heats of formation. (Hint: See Sample Problem 17-2.)

a. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

b. $Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(g)$

c. $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

22. Calculate the standard heats of reaction for combustion reactions in which ethane, C_2H_6, and benzene, C_6H_6, are the respective reactants and $CO_2(g)$ and $H_2O(l)$ are the products in each. Solve each by combining the known thermochemical equations using the ΔH_f^0 values in Appendix Table A-14 (page 902). Verify the result by using the general equation for finding heats of reaction from heats of formation.

a. $C_2H_6(g) + O_2(g) \longrightarrow$

b. $C_6H_6(l) + O_2(g) \longrightarrow$

23. The heat of formation of ethanol, C_2H_5OH, is -277.0 kJ/mol at 298.15 K. Calculate the heat of combustion of one mole of ethanol, assuming that the products are $CO_2(g)$ and $H_2O(l)$. (Hint: See Sample Problem 17-3.)

Entropy and Free Energy

24. Based on the following values, compute ΔG values for each reaction and predict whether the reaction will occur spontaneously. (Hint: See Sample Problem 17-4.)

a. $\Delta H = +125\ \frac{kJ}{mol}$, $T = 293\ K$, $\Delta S = 0.0350\ \frac{kJ}{(mol \cdot K)}$

b. $\Delta H = -85.2\ \frac{kJ}{mol}$, $T = 127°C$, $\Delta S = 0.125\ \frac{kJ}{(mol \cdot K)}$

c. $\Delta H = -275\ \frac{kJ}{mol}$, $T = 773\ K$, $\Delta S = 0.450\ \frac{kJ}{(mol \cdot K)}$

25. The ΔS^0 for the reaction shown, at 298.15 K, is 0.003 00 kJ/(mol•K). Calculate the ΔG^0 for this reaction, and determine whether it will occur spontaneously at 298.15 K.

$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.51\ kJ$

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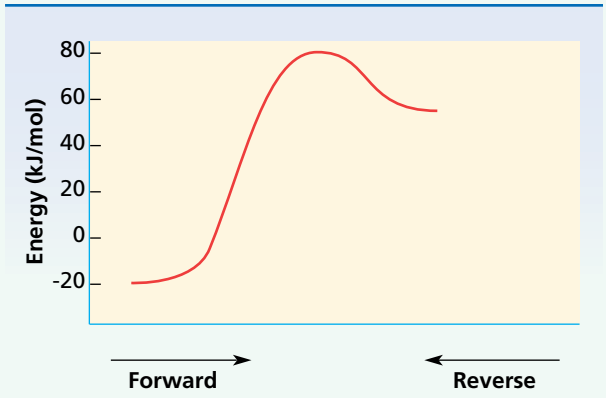
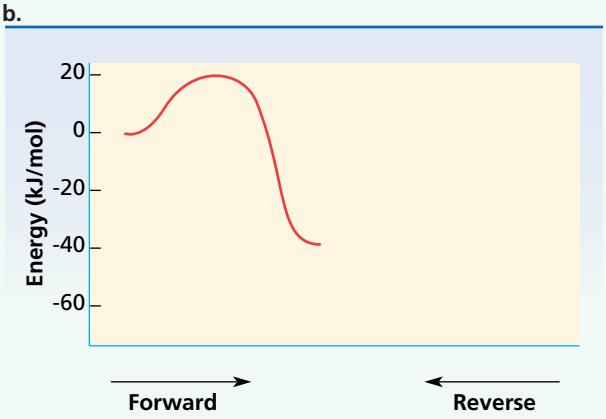
Reaction Diagrams

26. For each of the energy diagrams provided below, label the reactants, products, ΔE, E_a, and E_a'. Also determine the values of ΔE for the forward and reverse reactions, and the values of E_a and E_a'. (Hint: See Sample Problem 17-5.)

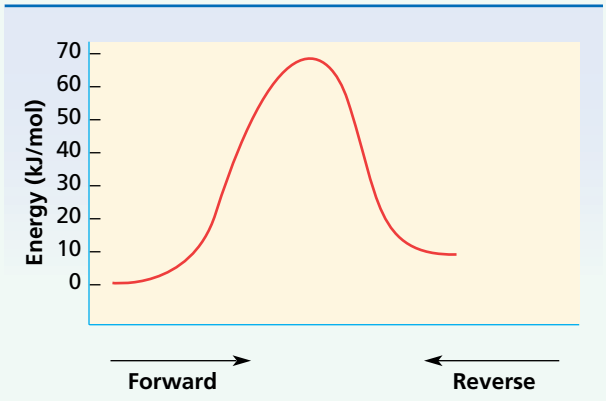
a.



b.



c.



27. Draw and label energy diagrams depicting the following reactions, and determine all remaining values. Place the reactants at energy level zero.

a. $\Delta E_{forward} = -10$ kJ/mol $\quad E_a' = 40$ kJ/mol
b. $\Delta E_{forward} = -95$ kJ/mol $\quad E_a = 20$ kJ/mol
c. $\Delta E_{reverse} = -40$ kJ/mol $\quad E_a' = 30$ kJ/mol

Rate Law

28. Determine the overall balanced equation for a reaction having the following proposed mechanism and write an acceptable rate law. (Hint: See Sample Problem 17-6.)

Step 1: $B_2 + B_2 \longrightarrow E_3 + D$ slow
Step 2: $E_3 + A \longrightarrow B_2 + C_2$ fast

29. A reaction involving reactants A and B is found to occur in the one-step mechanism: $2A + B \longrightarrow A_2B$. Write the rate law for this reaction, and predict the effect of doubling the concentration of either reactant on the overall reaction rate. (Hint: See Sample Problem 17-7.)

30. A chemical reaction is expressed by the balanced chemical equation $A + 2B \longrightarrow C$. Using the data below, answer the following:

a. Determine the rate law for the reaction.
b. Calculate the value of the specific rate constant.
c. If the initial concentrations of both A and B are 0.30 M, at what initial rate is C formed?

Three reaction-rate experiments yield the following data.

Experiment number	Initial [A]	Initial [B]	Initial rate of formation of C
1	0.20 M	0.20 M	2.0×10^{-4} M/min
2	0.20 M	0.40 M	8.0×10^{-4} M/min
3	0.40 M	0.40 M	1.6×10^{-3} M/min

MIXED REVIEW

31. When graphite reacts with hydrogen at 300 K, ΔH is –74.8 kJ/mol and ΔS is –0.0809 kJ/(mol•K). Will this reaction occur spontaneously?

32. How might you change reaction conditions to induce an endothermic reaction that does not occur naturally?

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33. The standard heat of formation for sulfur dioxide gas is –296.8 J/(mol•K). Calculate the amount of energy given off in kJ when 30.0 g of $SO_2(g)$ is formed from its elements.

34. The thermite reaction used in some welding applications has the following enthalpy and entropy changes at 298.15 K. Assuming ΔS and ΔH are constant, calculate ΔG at 448 K.

$Fe_2O_3 + 2Al(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$

$\Delta H^o = -851.5$ kJ/mol $\quad \Delta S^o = -38.5$ J/(mol•K)

35. Draw and label energy diagrams depicting the following reactions, and determine all remaining values. Place the reactants at energy level zero.

a. $\Delta E = +30$ kJ/mol $\quad E_a' = 20$ kJ/mol

b. $\Delta E = -30$ kJ/mol $\quad E_a = 20$ kJ/mol

36. A particular reaction is found to have the following rate law.

$$R = k[A][B]^2$$

How is the rate affected by each of the following changes?

a. the initial concentration of A is cut in half

b. the initial concentration of B is tripled

c. the concentration of A is doubled, but the concentration of B is cut in half

d. a catalyst is added

37. Rewrite each equation below with the ΔH value included in either the reactants or products, and identify the reaction as endothermic or exothermic.

a. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g); \Delta H = -197.8$ kJ/mol

b. $2NO_2(g) \longrightarrow 2NO(g) + O_2(g); \Delta H = +114.2$ kJ/mol

c. $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l); \Delta H = -1411.0$ kJ/mol

38. For each of the following pairs, choose the substance or process you would expect to react more rapidly.

a. granulated sugar or powdered sugar

b. zinc in HCl at 298.15 K or zinc in HCl at 410 K

c. 5 g of thick platinum wire or 5 g of thin platinum wire

39. Calculate the change in enthalpy for the following reaction.

$$4FeO(s) + O_2(g) \longrightarrow 2Fe_2O_3(s)$$

Use the heat-of-formation data listed in Appendix Table A-14.

CRITICAL THINKING

40. Predicting Outcomes The balanced equation for a rapid homogeneous reaction between two gases is as follows: $4A + B \longrightarrow 2C + 2D$. Since the simultaneous collision of four molecules of one reactant with one molecule of the other reactant is extremely improbable, what would you predict about the nature of the reaction mechanism for this reaction system?

41. Evaluating Ideas

a. How can you justify calling the reaction pathway that is shown in Figure 17-10 the minimum-energy pathway for reaction?

b. What significance is associated with the maximum-energy region of this minimum-energy pathway?

42. Applying Models Explain why there is a danger of explosion in places such as coal mines, saw mills, and grain elevators, where large amounts of dry, powdered combustible materials are present.

43. Evaluating Methods What property would you measure in order to determine the reaction rate for the following reaction? Justify your choice.

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

TECHNOLOGY & LEARNING

44. Graphing Calculator Calculating the Free-Energy Change

The graphing calculator can run a program that calculates the free-energy change, given the temperature, T, change in enthalpy, ΔH, and change in entropy, ΔS. Given that the temperature is 298 K, the change in enthalpy is 131.3 kJ/mol, and the change in entropy is 0.134 kJ/(mol•K), you can calculate free-energy change in kJ/mol. Then use the program to make calculations.

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Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. What is the free energy change given a temperature of 300 K, a change in enthalpy of 132 kJ/mol, and a change in entropy of 0.086 kJ/(mol•K)?
b. What is the free energy change given a temperature of 288 K, a change in enthalpy of 115 kJ/mol, and a change in entropy of 0.113 kJ/(mol•K)?
c. What is the free energy change given a temperature of 298 K, a change in enthalpy of 181 kJ/mol, and a change in entropy of 0.135 kJ/(mol•K)?

RESEARCH & WRITING

45. Obtain information on alternative units of measure used to express values of heat and other forms of energy. Also, find out how the quantities relate to SI metric units. Include information specifically on English units, such as the British Thermal Unit (BTU), and on typical BTU ratings of household appliances. Calculate how these ratings would be expressed in joules instead.

46. Look for situations around your house in which processes are speeded up by an increase in temperature or slowed down by a decrease in temperature. Make a list, and discuss the different processes.

ALTERNATIVE ASSESSMENT

47. Performance Design a simple calorimeter investigation to determine the molar heat of fusion of water. Use the following materials: a large plastic-foam cup with cover, a thermometer, a balance, water at room temperature, and an ice cube. Allow your teacher to review your design. Then carry out the investigation, and write a laboratory report including your calculations and a comparison of your quantitative results with known values. Try to account for any disagreements between the experimental and actual values.

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CHAPTER 18

Chemical Equilibrium

The creation of stalactites and stalagmites is the result of a reversible chemical reaction.

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SECTION 18-1

The Nature of Chemical Equilibrium

Objectives

- Define *chemical equilibrium.*
- Explain the nature of the equilibrium constant.
- Write chemical equilibrium expressions and carry out calculations involving them.

In systems that are in equilibrium, opposing processes occur at the same time and at the same rate. For example, when an excess of sugar is placed in water, sugar molecules go into solution. At equilibrium, molecules of sugar are crystallizing at the same rate that molecules from the crystal are dissolving. The rate of evaporation of a liquid in a closed vessel can eventually be equaled by the rate of condensation of its vapor. The resulting equilibrium vapor pressure is a characteristic of the liquid at the prevailing temperature. Le Châtelier's principle, which you read about in Chapter 12, can help predict the outcome of changes made to these equilibrium systems. The preceding examples are physical equilibria. The concept of equilibrium and Le Châtelier's principle also apply to chemical processes.

Reversible Reactions

Theoretically, every reaction can proceed in two directions, forward and reverse. Thus, essentially all chemical reactions are considered to be reversible under suitable conditions. *A chemical reaction in which the products can react to re-form the reactants is called a* **reversible reaction.**

Mercury(II) oxide decomposes when heated.

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

Mercury and oxygen combine to form mercury(II) oxide when heated gently.

$$2Hg(l) + O_2(g) \xrightarrow{\Delta} 2HgO(s)$$

Figure 18-1 shows both of these reactions taking place. Suppose mercury(II) oxide is heated in a closed container from which neither the mercury nor the oxygen can escape. Once decomposition has begun, the mercury and oxygen released can recombine to form mercury(II) oxide again. Thus, both reactions can proceed at the same time. Under these conditions, the rate of the composition reaction will eventually equal that of the decomposition reaction. At equilibrium, mercury and oxygen will

FIGURE 18-1 When heated, mercury(II) oxide decomposes into the elements from which it was formed. Liquid mercury reacts with oxygen to re-form mercury(II) oxide. Together these reactions represent a reversible chemical process.

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combine to form mercury(II) oxide at the same rate that mercury(II) oxide decomposes into mercury and oxygen. The amounts of mercury(II) oxide, mercury, and oxygen can then be expected to remain constant as long as these conditions persist. At this point, a state of dynamic equilibrium has been reached between the two chemical reactions. Both reactions continue, but there is no net change in the composition of the system. *A reversible chemical reaction is in* **chemical equilibrium** *when the rate of its forward reaction equals the rate of its reverse reaction and the concentrations of its products and reactants remain unchanged.* The chemical equation for the reaction at equilibrium is written using double arrows to indicate the overall reversibility of the reaction.

$$2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$$

Equilibrium, a Dynamic State

Many chemical reactions are reversible under ordinary conditions of temperature and concentration. They will reach a state of equilibrium unless at least one of the substances involved escapes or is removed from the reaction system. In some cases, however, the forward reaction is nearly completed before the rate of the reverse reaction becomes high enough to establish equilibrium. Here, the products of the forward reaction are favored, meaning that at equilibrium there is a higher concentration of products than of reactants. The favored reaction that produces this situation is referred to as a reaction to the right because the convention for writing chemical reactions is that *left-to-right* is forward and *right-to-left* is reverse. An example of such a system is the dissociation of hydrobromic acid in aqueous solution.

$$HBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Br^-(aq)$$

Notice that the equation is written showing an inequality of the two arrow lengths. The forward reaction is represented by the longer arrow to imply that products are favored in this reaction.

In other cases, the forward reaction is barely under way when the rate of the reverse reaction becomes equal to that of the forward reaction, and equilibrium is established. In these cases, the products of the reverse reaction are favored and the original reactants are formed. That is, at equilibrium there is a higher concentration of reactants than of products. The favored reaction that produces this situation is referred to as a reaction to the left. An example of such a system is the acid-base reaction between carbonic acid and water.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

In still other cases, both forward and reverse reactions occur to nearly the same extent before chemical equilibrium is established. Neither

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reaction is favored, and considerable concentrations of both reactants and products are present at equilibrium. An example is the dissociation of sulfurous acid in water.

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$$

Chemical reactions ordinarily are used to convert available reactants into more desirable products. Chemists try to convert as much of these reactants as possible into products. The extent to which reactants are converted to products can be determined from the numerical value of the equilibrium constant.

The Equilibrium Expression

Suppose two substances, A and B, react to form products C and D. In turn, C and D react to produce A and B. Under appropriate conditions, equilibrium occurs for this reversible reaction. This hypothetical equilibrium reaction is described by the following general equation.

$$nA + mB \rightleftharpoons xC + yD$$

Initially, the concentrations of C and D are zero and those of A and B are maximum. Figure 18-2 shows that over time the rate of the forward reaction decreases as A and B are used up. Meanwhile, the rate of the reverse reaction increases as C and D are formed. When these two reaction rates become equal, equilibrium is established. The individual concentrations of A, B, C, and D undergo no further change if conditions remain the same.

After equilibrium is attained, the concentrations of products and reactants remain constant, so a ratio of their concentrations should also

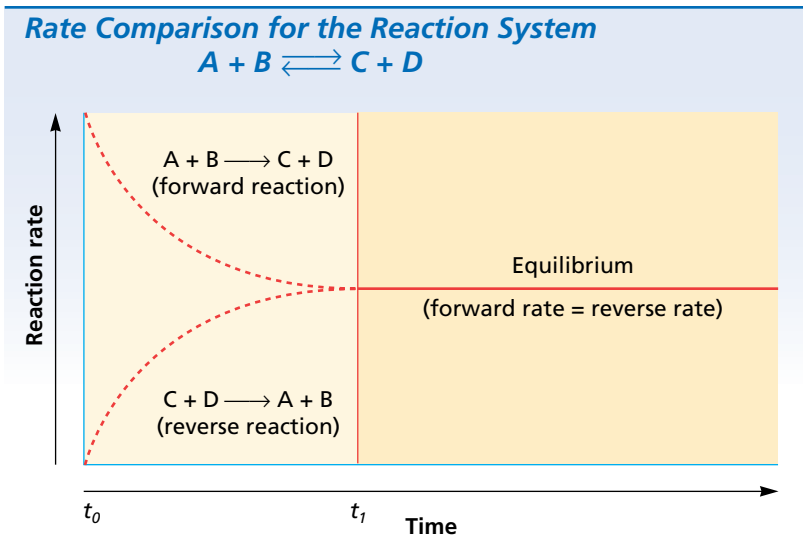

FIGURE 18-2 Shown are reaction rates for the hypothetical equilibrium reaction system $A + B \rightleftharpoons C + D$. From the time A and B are mixed together at t_0, the rate of the forward reaction declines and the rate of the reverse reaction increases until both forward and reverse reaction rates are equal at t_1, when the equilibrium condition begins.

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remain constant. The ratio of the mathematical product $[C]^x \times [D]^y$ to the mathematical product $[A]^n \times [B]^m$ for this reaction has a definite value at a given temperature. It is the equilibrium constant of the reaction and is designated by the letter *K*. The following equation describes the equilibrium constant for the hypothetical equilibrium system. [C] indicates the concentration of C in moles per liter. The concentrations of the other substances are indicated similarly.

$$K = \frac{[C]^x[D]^y}{[A]^n[B]^m}$$

The concentrations of substances on the right side of the chemical equation appear in the numerator of the equilibrium ratio, with each concentration raised to a power equal to the coefficient of that substance in the chemical equation. These substances are the products of the forward reaction. The concentrations of substances on the left side of the chemical equation are found in the denominator of the equilibrium ratio, with each concentration raised to a power equal to the coefficient of that substance in the chemical equation. These substances are the reactants of the forward reaction. The constant *K* is independent of the initial concentrations. It is, however, dependent on the temperature of the system.

The Equilibrium Constant

The numerical value of *K* for a particular equilibrium system is obtained experimentally. The chemist must analyze the equilibrium mixture and determine the concentrations of all substances. The value of *K* for a given equilibrium reaction at a given temperature shows the extent to which the reactants are converted into the products of the reaction. If *K* is equal to 1, the products of the concentrations raised to the appropriate power in the numerator and denominator have the same value. Therefore, at equilibrium, there are roughly equal concentrations of reactants and products. If the value of *K* is low, the forward reaction occurs only very slightly before equilibrium is established, and the reactants are favored. A high value of *K* indicates an equilibrium in which the original reactants are largely converted to products. Only the concentrations of substances that can actually change are included in *K*. This means that *pure* solids and liquids are omitted because their concentrations cannot change.

In general, then, *the* **equilibrium constant,** *K, is the ratio of the mathematical product of the concentrations of substances formed at equilibrium to the mathematical product of the concentrations of reacting substances. Each concentration is raised to a power equal to the coefficient of that substance in the chemical equation. The equation for K is sometimes referred to as the* **chemical-equilibrium expression.**

The H_2, I_2, HI Equilibrium System

Consider the reaction between H_2 and I_2 vapor in a sealed flask at an elevated temperature. The rate of reaction can be followed by observing the rate at which the violet color of the iodine vapor diminishes, as

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shown in Figure 18-3. Suppose the hydrogen gas is present in excess and the reaction continues until all the iodine is used up. The color of the flask's contents, provided by the iodine gas, will gradually become less intense because the product, hydrogen iodide, HI, and the excess hydrogen are both colorless gases.

In actuality, the color fades to a constant intensity but does not disappear because the reaction is reversible. Hydrogen iodide decomposes to re-form hydrogen and iodine. The rate of this reverse reaction increases as the concentration of hydrogen iodide increases. The rate of the forward reaction decreases accordingly. The concentrations of hydrogen and iodine decrease as they are used up. As the rates of the opposing reactions become equal, an equilibrium is established. The constant color achieved indicates that equilibrium exists among hydrogen, iodine, and hydrogen iodide. The net chemical equation for the reaction system at equilibrium follows.

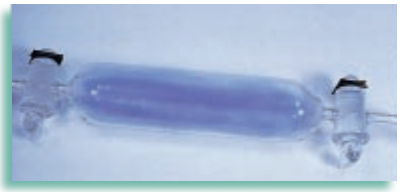
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

From this chemical equation, the following chemical-equilibrium expression can be written. The concentration of HI is raised to the power of 2 because the coefficient of HI in the balanced chemical equation is 2.

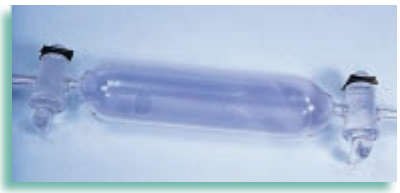
$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Chemists have carefully measured the concentrations of H_2, I_2, and HI in equilibrium mixtures at various temperatures. In some experiments, the flasks were filled with hydrogen iodide at known pressure. The flasks were held at fixed temperatures until equilibrium was established. In other experiments, hydrogen and iodine were the original substances. Experimental data, together with the calculated values for K, are listed in Table 18-1. Experiments 1 and 2 began with hydrogen iodide. Experiments 3 and 4 began with hydrogen and iodine. Note the close agreement obtained for the numerical values of the equilibrium constant in all cases.

At 425°C, the equilibrium constant for this equilibrium reaction system has the average value of 54.34. This value for K should hold for any system of H_2, I_2, and HI at equilibrium at this temperature. If the



(a)



(b)

(c)

FIGURE 18-3 Hydrogen iodide gas is produced from gaseous hydrogen and iodine. The violet color of iodine gas (a) becomes fainter as the reaction consumes the iodine (b). The violet does not disappear but reaches a constant intensity when the reaction reaches equilibrium (c).

TABLE 18-1 *Typical Equilibrium Concentrations of H_2, I_2, and HI in mol/L at 425°C*

Experiment	$[H_2]$	$[I_2]$	$[HI]$	$K = \frac{[HI]^2}{[H_2][I_2]}$
1	0.4953×10^{-3}	0.4953×10^{-3}	3.655×10^{-3}	54.46
2	1.141×10^{-3}	1.141×10^{-3}	8.410×10^{-3}	54.33
3	3.560×10^{-3}	1.250×10^{-3}	15.59×10^{-3}	54.62
4	2.252×10^{-3}	2.336×10^{-3}	16.85×10^{-3}	53.97

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calculation for K yields a different result, there must be a reason. Either the H_2, I_2, and HI system has not reached equilibrium or the system is not at 425°C.

The balanced chemical equation for an equilibrium system helps establish the expression for the equilibrium constant. The data in Table 18-1 show that the validity of this expression is confirmed when the actual values of the equilibrium concentrations of reactants and products are determined experimentally. The values of K are calculated from these concentrations. No information concerning the kinetics of the reacting systems is required.

Once the value of the equilibrium constant is known, the equilibrium-constant expression can be used to calculate concentrations of reactants or products at equilibrium. Suppose an equilibrium system at 425°C is found to contain 0.015 mol/L each of H_2 and I_2. To find the concentration of HI in this system, the chemical equilibrium expression can be rearranged as shown in the two equations that follow.

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

$$[HI] = \sqrt{K[H_2][I_2]}$$

Using the known K value and the given concentrations for H_2 and I_2, the equation can be solved for [HI].

$$[HI] = \sqrt{0.015 \times 0.015 \times 54.34}$$
$$= 0.11 \text{ mol/L}$$

SAMPLE PROBLEM 18-1

An equilibrium mixture of N_2, O_2, and NO gases at 1500 K is determined to consist of 6.4×10^{-3} mol/L of N_2, 1.7×10^{-3} mol/L of O_2, and 1.1×10^{-5} mol/L of NO. What is the equilibrium constant for the system at this temperature?

SOLUTION

1 ANALYZE

Given: $[N_2] = 6.4 \times 10^{-3}$ mol/L
$[O_2] = 1.7 \times 10^{-3}$ mol/L
$[NO] = 1.1 \times 10^{-5}$ mol/L

Unknown: K

2 PLAN

The balanced chemical equation is $N_2(g) + O_2(g) \rightleftarrows 2NO(g)$.

The chemical equilibrium expression is $K = \frac{[NO]^2}{[N_2][O_2]}$.

3 COMPUTE

Substitute the given values for the concentrations into the equilibrium expression.

$$K = \frac{(1.1 \times 10^{-5} \text{ mol/L})^2}{(6.4 \times 10^{-3} \text{ mol/L})(1.7 \times 10^{-3} \text{ mol/L})} = 1.1 \times 10^{-5}$$

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4 EVALUATE The answer has the correct number of significant figures and is close to an estimated value of 8×10^{-6}, calculated as $\frac{1 \times 10^{-10}}{(6 \times 10^{-3})(2 \times 10^{-3})}$.

PRACTICE

1. At equilibrium a mixture of N_2, H_2, and NH_3 gas at 500°C is determined to consist of 0.602 mol/L of N_2, 0.420 mol/L of H_2, and 0.113 mol/L of NH_3. What is the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at this temperature?

   Answer 0.286

2. The reaction $AB_2C(g) \rightleftharpoons B_2(g) + AC(g)$ reached equilibrium at 900 K in a 5.00 L vessel. At equilibrium 0.084 mol of AB_2C, 0.035 mol of B_2, and 0.059 mol of AC were detected. What is the equilibrium constant at this temperature for this system?

   Answer 4.9×10^{-3}

3. At equilibrium a 1.0 L vessel contains 20.0 mol of H_2, 18.0 mol of CO_2, 12.0 mol of H_2O, and 5.9 mol of CO at 427°C. What is the value of K at this temperature for the following reaction?

   $$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

   Answer 0.20

4. A reaction between gaseous sulfur dioxide and oxygen gas to produce gaseous sulfur trioxide takes place at 600°C. At that temperature, the concentration of SO_2 is found to be 1.50 mol/L, the concentration of O_2 is 1.25 mol/L, and the concentration of SO_3 is 3.50 mol/L. Using the balanced chemical equation, calculate the equilibrium constant for this system.

   Answer 4.36

SECTION REVIEW

1. What is meant by *chemical equilibrium*?
2. What is an equilibrium constant?
3. How does the value of an equilibrium constant relate to the relative quantities of reactants and products at equilibrium?
4. What is meant by a *chemical-equilibrium expression*?
5. Hydrochloric acid, HCl, is a strong acid that dissociates completely in water to form H_3O^+ and Cl^-. Would you expect the value of K for the reaction $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ to be 1×10^{-2}, 1×10^{-5}, or "very large"? Justify your answer.
6. Write the chemical-equilibrium expression for the reaction $4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$.
7. At equilibrium at 2500 K, [HCl] = 0.0625 mol/L and $[H_2] = [Cl_2] = 0.0045$ mol/L for the reaction $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$. Find the value of K.
8. An equilibrium mixture at 425°C is found to consist of 1.83×10^{-3} mol/L of H_2, 3.13×10^{-3} mol/L of I_2, and 1.77×10^{-2} mol/L of HI. Calculate the equilibrium constant, K, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.
9. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 425°C, calculate [HI], given $[H_2] = [I_2] = 4.79 \times 10^{-4}$ mol/L and $K = 54.3$.

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Fixing the Nitrogen Problem

HISTORICAL PERSPECTIVE

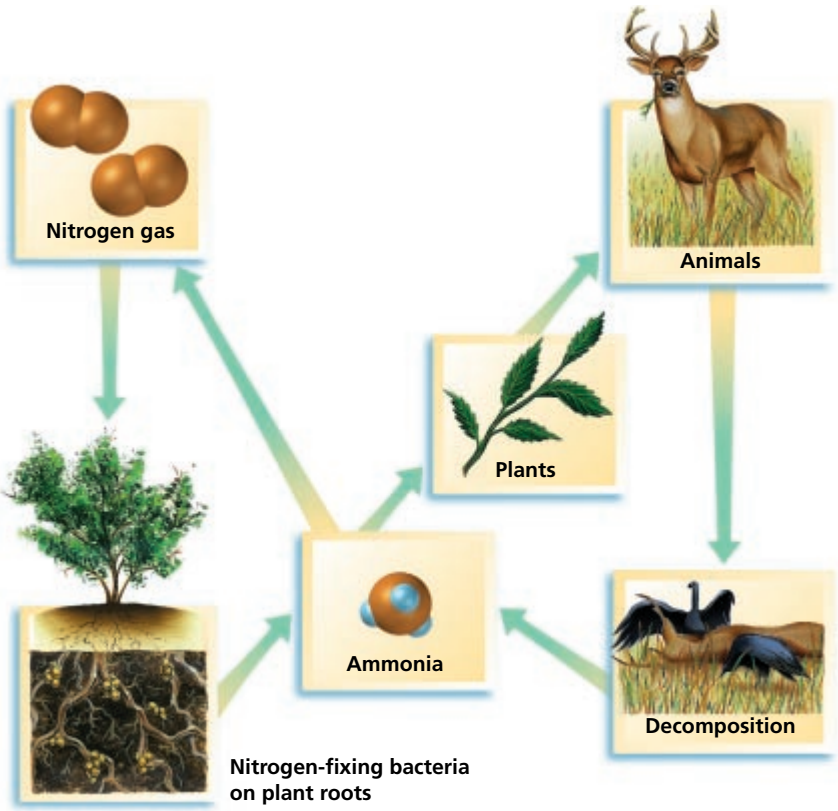
Each year, the chemical industry synthesizes tons of nitrogenous fertilizer, increasing agricultural production around the globe. But prior to 1915, humans had to rely solely on natural resources for fertilizer, and the dwindling supply of these materials caused widespread fear of world starvation. A crisis was averted, however, through the discovery of an answer to the "nitrogen problem," a term used at the time to describe the shortage of useful nitrogen despite its abundance in the atmosphere.

The Malthusian Threat

In 1798, Thomas Malthus published his famous "Essay on Population," a report predicting that the world's food supplies could not keep up with the growing human population and that famine, death, and misery were inevitable. Malthus's warning seemed to be echoed in the 1840s by the great Irish potato famine. In fact, the rest of Europe likely would have suffered serious food shortages as well had crop yields per acre not been increased through the use of fertilizers containing nitrogen.

Few living things can utilize the gas that forms 78 percent of the atmosphere; they need nitrogen that has been combined with other elements, or "fixed," to survive.

But soil often lacks sufficient amounts of the organisms that fix nitrogen for plants, so fertilizers containing usable nitrogen compounds are added. In 1898, two-thirds of the world's supply of these compounds came from Chile, where beds of sodium nitrate, or Chilean saltpeter, were abundant.



Nitrogen is released when living things die and also from animal wastes and plant material. A few kinds of bacteria are able to break the bond holding the nitrogen molecule together, freeing the nitrogen atoms to combine with hydrogen to form ammonia. Plants can absorb the nitrogen in this form from the soil. Animals then benefit from the nitrogen by eating the plants.

But, as the chemist William Crookes emphasized in his speech to the British Association that year, these reserves were limited; it was up to his colleagues to discover alternatives and prevent Malthus's dire forecast from coming true:

> *It is the chemist who must come to the rescue of the threatened communities.*

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The Haber-Nernst Controversy

As early as the 1890s, chemists had shown that ammonia, a practical source of fixed nitrogen, could be synthesized at high temperatures and at atmospheric pressure from elemental hydrogen and nitrogen. The problem was that the end-product was present in such minute amounts that the process was not industrially practical.

In 1904, the German chemist Fritz Haber seemed to confirm this assessment. He tried reacting hydrogen and nitrogen at temperatures of up to 1020°C using pure iron as well as other metals as a catalyst. He found that the amount of ammonia was a mere 0.005–0.012% at equilibrium. Thus, he concluded:

> *From dull red heat . . . no catalyst can produce more than traces of ammonia . . . and even at . . . increased pressures the position of the equilibrium must remain very unfavorable.*

Haber had apparently closed the door on the synthesis of ammonia from its elements. But in 1906, Walther Nernst, using his new heat theorem, calculated the reaction's theoretical ammonia concentration at equilibria corresponding to several pressures. He found that his value at atmospheric pressure disagreed significantly with Haber's, and he publicly challenged Haber's values.

Haber was convinced that he was right. Applying Le Châtelier's principle, he ran the reaction at increased pressure to attain an amount of ammonia that could be measured more accurately.

Haber and his assistants confirmed their original findings, and Nernst later conceded a mathematical error. But more important, the new round of experiments indicated that a reasonable amount of ammonia might be attained at pressures of 200 atm (402 kPa) using a uranium or osmium catalyst.

Today ammonia is produced on an industrial scale in plants like this one.

Scaling Up

Large-scale equipment that could withstand such high pressures was unheard of at the time, and osmium and uranium were far too scarce to be cost-effective for industry. Nevertheless, in 1909, the German firm BASF bought the rights to Haber's findings and put its gifted chemical engineer Karl Bosch in charge of creating an industrial-scale system that would make the process profitable.

After nearly five years, Bosch and the company's chief chemist, Alwin Mittasch, succeeded in developing a suitable reactor that could handle the reaction's high pressures. They also discovered that a catalyst of iron containing small amounts of impurities was an effective replacement for the rare metals used by Haber. Haber was impressed:

> *It is remarkable how matter . . . reveals new facets. Iron . . . studied a hundred times in the pure state, now works in the impure state.*

An Eerie Epilogue

By September of 1913, BASF was producing 20 metric tons of ammonia a day using the Haber-Bosch process. Eventually, enough ammonia was produced by the chemical industry to free Germany and the world of dependence on Chilean saltpeter for fertilizer. Chemists had thwarted the Malthusian threat. Yet, the victory proved bittersweet; the new ammonia synthesis also became the basis of the production of nitric acid, used to make many of the explosives employed in the wars that rocked Europe and the rest of the globe in the first half of the twentieth century.

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SECTION 18-2

Shifting Equilibrium

Objectives

- Discuss the factors that disturb equilibrium.
- Discuss conditions under which reactions go to completion.
- Describe the common-ion effect.

CHEMISTRY INTERACTIVE TUTOR
Module 7: Equilibrium

In systems that have attained chemical equilibrium, the forward and reverse reactions are proceeding at equal rates. Any change that alters the rates of these reactions disturbs the original equilibrium. The system then seeks a new equilibrium state. By shifting an equilibrium in the desired direction, chemists can often improve the yield of the product they are seeking.

Predicting the Direction of Shift

Le Châtelier's principle provides a means of predicting the influence of stress factors on equilibrium systems. As you may recall from Chapter 12, Le Châtelier's principle states that *if a system at equilibrium is subjected to a stress, the equilibrium is shifted in the direction that tends to relieve the stress.* This principle is true for all dynamic equilibria, chemical as well as physical. Changes in pressure, concentration, and temperature illustrate the application of Le Châtelier's principle to chemical equilibrium.

Changes in Pressure

A change in pressure affects only equilibrium systems in which gases are involved. For changes in pressure to affect the system, the total number of moles of gas on the left side of the equation must be different from the total number of moles on the right side of the equation. For example, the balanced chemical equation for the decomposition of solid $CaCO_3$ given on page 564 indicates that 0 mol reactant gases produce 1 mol of product gases. The change in moles is 1. Therefore, a high pressure favors the reverse reaction because fewer CO_2 molecules are produced. A similar argument can explain the increased production of CO_2 that accompanies a low system pressure.

Next let us consider the Haber process for the synthesis of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

This situation is somewhat different. First consider an increase in pressure as the applied stress. Can the system shift in a way that reduces the stress? Yes. An increase in pressure causes increases in the concentrations of all species. The system can reduce the number of molecules, and hence the total pressure, by shifting the equilibrium to the right. For each four molecules of reactants there are two molecules of products. By producing more NH_3, and using up N_2 and H_2, the system can reduce

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the number of molecules. This leads to a decrease in pressure. However, the new equilibrium pressure is still higher than before, although not as high as the pressure caused by the initial stress.

An increase in pressure on confined gases causes an increase in the concentrations of these gases. So changes in pressure may shift the equilibrium position, but they do not affect the value of the equilibrium constant.

Ammonia produced in the Haber process is continuously removed by condensation to liquid. This condensation removes most of the product from the gas phase in which the reaction occurs. The resulting decrease in the partial pressure of NH_3 gas in the reaction vessel is the same as a decrease in product concentration and shifts the equilibrium to the right.

The introduction of an inert gas, such as helium, into the reaction vessel for the synthesis of ammonia increases the total pressure in the vessel. But it does not change the partial pressures of the reaction gases present. Therefore, increasing pressure by adding a gas that is not a reactant or a product *cannot* affect the equilibrium position of the reaction system.

Changes in Concentration

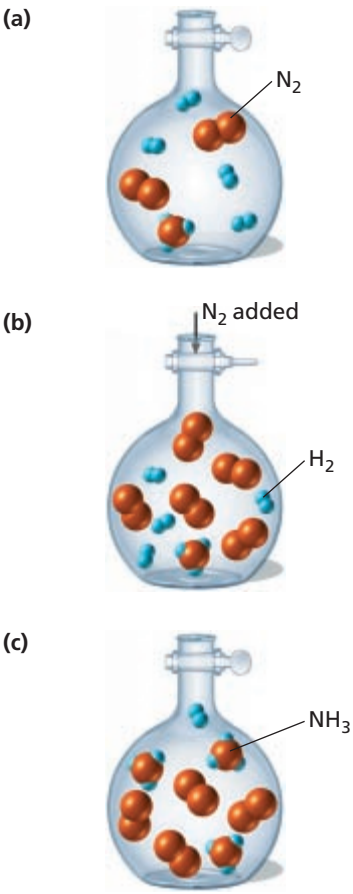
An increase in the concentration of a reactant is a stress on the equilibrium system. It causes an increase in collision frequency and, generally, an increase in reaction rate. Consider the following hypothetical reaction.

$$A + B \rightleftharpoons C + D$$

An increase in the concentration of A shifts the equilibrium to the right. Both A and B are used up faster, and more of C and D is formed. The equilibrium is reestablished with a lower concentration of B. The equilibrium has shifted to reduce the stress caused by the increase in concentration of A. Figure 18-4 illustrates the effect on a system in equilibrium produced by increasing the concentration of a reactant. Similarly, an increase in the concentration of B drives the reaction to the right. An increase in the concentration of either C or D increases the rate of the reverse reaction, and the equilibrium shifts to the left. A decrease in the concentration of C or D has the same effect on the position of the equilibrium as does an increase in the concentration of A or B; the equilibrium shifts to the right.

Changes in concentration have no effect on the value of the equilibrium constant. This is because such changes have an equal effect on the numerator and the denominator of the chemical equilibrium expression. Thus, all concentrations give the same value or numerical ratio for the equilibrium constant when equilibrium is reestablished.

Many chemical processes involve heterogeneous reactions in which the reactants and products are in different phases. The *concentrations* of pure substances in solid and liquid phases are not changed by adding or removing quantities of the substance. This is because concentration is density-dependent, and the density of these phases is constant, regardless of the total amounts present. *A pure substance in a condensed phase, solid or liquid, can be eliminated from the expression for the*



$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

FIGURE 18-4 (a) H_2, N_2, and NH_3 are in equilibrium within a closed system. (b) Addition of more N_2 causes a stress on the initial equilibrium. (c) The new equilibrium position for this system. There is now a higher concentration of N_2, a lower concentration of H_2, and a higher concentration of NH_3.

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equilibrium constant. The concentration of the pure solid or liquid is set equal to 1 in the equilibrium expression, signifying that the concentration is assumed to remain unchanged in the equilibrium system.

The following equation describes the equilibrium system established by the decomposition of solid calcium carbonate.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The products are a solid and a gas, leading to the following expression for the equilibrium constant.

$$K = \frac{[CaO][CO_2]}{[CaCO_3]} = \frac{[1][CO_2]}{[1]} = [CO_2]$$

Carbon dioxide is the only substance in the system subject to changes in concentration. Because it is a gas, the system is affected by pressure changes.

Changes in Temperature

Reversible reactions are exothermic in one direction and endothermic in the other. The effect of changing the temperature of an equilibrium mixture depends on which of the opposing reactions is endothermic and which is exothermic.

According to Le Châtelier's principle, the addition of heat shifts the equilibrium so that heat is absorbed. This favors the endothermic reaction. The removal of heat favors the exothermic reaction. A rise in temperature increases the rate of any reaction. In an equilibrium system, however, the rates of the opposing reactions are raised unequally. Thus, the value of the equilibrium constant for a given system is affected by the temperature.

The synthesis of ammonia by the Haber process is exothermic, as indicated by the heat shown on the product side of the equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ kJ$$

A high temperature is not desirable because it favors the decomposition of ammonia, the endothermic reaction. At low temperatures, however, the forward reaction is too slow to be commercially useful. The temperature used represents a compromise between kinetic and equilibrium requirements. It is high enough that equilibrium is established rapidly but low enough that the equilibrium concentration of ammonia is significant. Moderate temperature (about 500°C) and very high pressure (700–1000 atm) produce a satisfactory yield of ammonia.

The production of colorless dinitrogen tetroxide gas, N_2O_4, from dark brown NO_2 gas is also an exothermic reaction. Figure 18-5 shows how temperature affects the equilibrium of this system. In this figure, all three flasks contain the same total mass of gas, a mixture of NO_2 and N_2O_4. In Figure 18-5(a) the temperature of the system is lowered to 0°C. This causes the equilibrium of the system to shift to the right, allowing more of the colorless N_2O_4 gas to form, which produces a light brown color.

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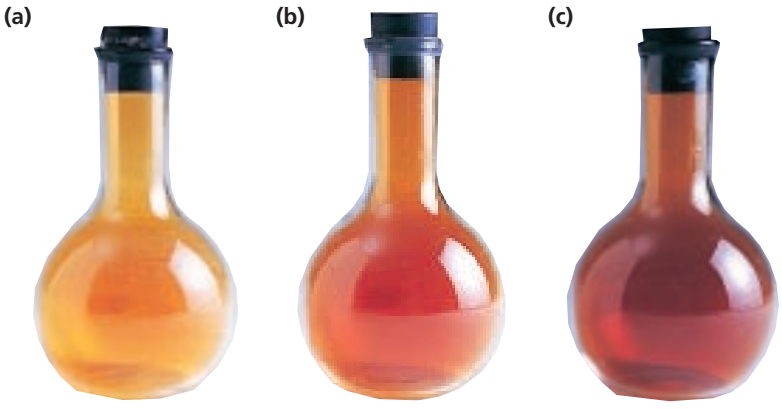

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

FIGURE 18-5 Different temperatures can cause an equilibrium system to shift and seek a new equilibrium position.

The system is at equilibrium at 25°C in Figure 18-5(b). The system contains an equilibrium mixture of NO_2 and N_2O_4, producing a medium brown color. As the temperature is raised to 100°C, as shown in Figure 18-5(c), the equilibrium shifts to the left, causing more of the dark brown NO_2 gas to form.

For an endothermic reaction, such as the decomposition of calcium carbonate, heat shows up on the reactant side of the equation.

$$556\ \text{kJ} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

An increase in temperature caused by adding heat to the system causes the value of K to increase and the equilibrium to shift to the right.

The reactions of the system are also accelerated by a suitable catalyst. However, catalysts have no effect on relative equilibrium amounts. They only affect the rates at which equilibrium is reached. This is because catalysts increase the rates of forward and reverse reactions in a system by equal factors. Therefore, they do not affect K.

Reactions That Go to Completion

Some reactions involving compounds formed by the chemical interaction of ions in solutions appear to go to completion in the sense that the ions are almost completely removed from solution. The extent to which reacting ions are removed from solution depends on the solubility of the compound formed and, if the compound is soluble, on the degree of ionization. Thus, a product that escapes as a gas, precipitates as a solid, or is only slightly ionized effectively removes from solution the bulk of the reacting ions that compose it. Consider some specific examples of situations in which such ionic reactions go to completion.

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Formation of a Gas

Unstable substances formed as products of ionic reactions decompose spontaneously. An example is carbonic acid, H_2CO_3, the acid in carbonated water, such as club soda, which yields a gas as a decomposition product.

$$H_2CO_3(aq) \longrightarrow H_2O(l) + CO_2(g)$$

This reaction goes practically to completion because one of the products, CO_2, escapes as a gas if the container is open to the air.

Formation of a Precipitate

When solutions of sodium chloride and silver nitrate are mixed, a white precipitate of silver chloride immediately forms, as shown in Figure 18-6. The overall ionic equation for this reaction follows.

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow Na^+(aq) + NO_3^-(aq) + AgCl(s)$$

If chemically equivalent amounts of the two solutes are used, only Na^+ ions and NO_3^- ions remain in solution in appreciable quantities. Almost all of the Ag^+ ions and Cl^- ions combine and separate from the solution as a precipitate of AgCl. This is because AgCl is only very sparingly soluble in water. It separates by precipitation from what turns out to be a saturated solution of its particles. The reaction thus effectively goes to completion because an essentially insoluble product is formed.

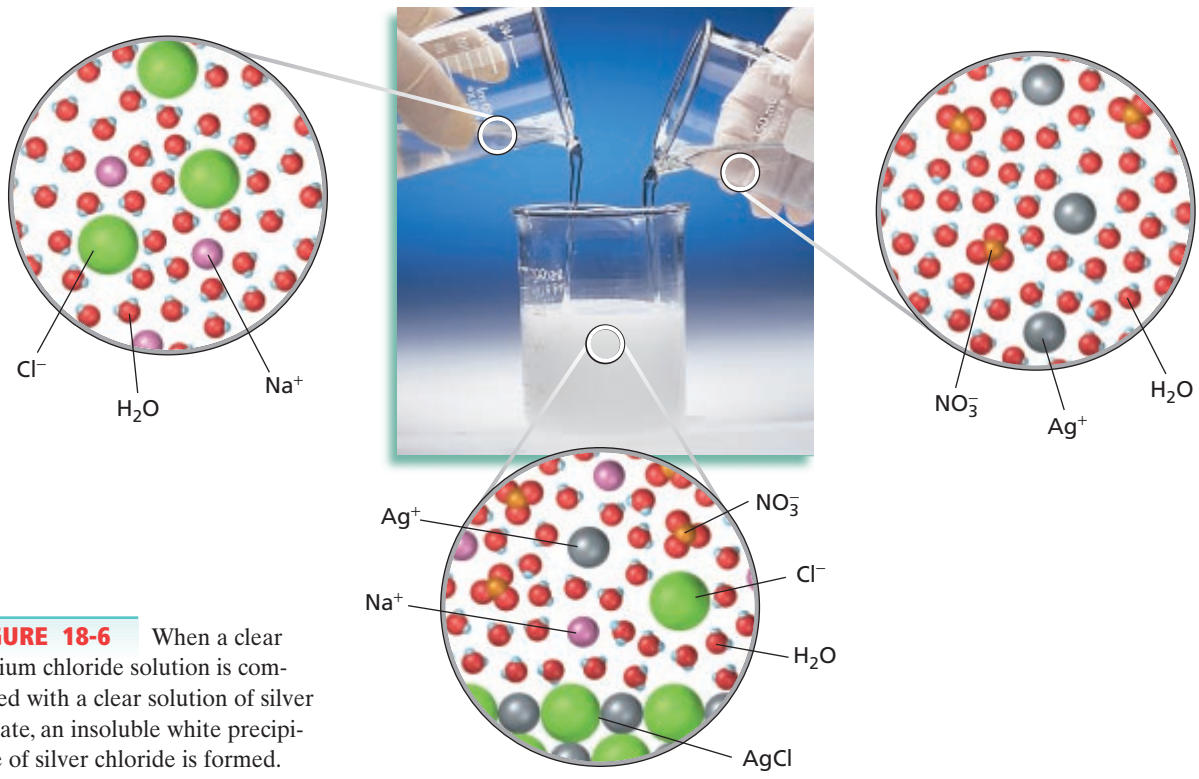

FIGURE 18-6 When a clear sodium chloride solution is combined with a clear solution of silver nitrate, an insoluble white precipitate of silver chloride is formed.

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Formation of a Slightly Ionized Product

Neutralization reactions between H_3O^+ ions from aqueous acids and OH^- ions from aqueous bases result in the formation of water molecules, which are only slightly ionized. A reaction between HCl and NaOH illustrates this process. Aqueous HCl supplies H_3O^+ ions and Cl^- ions to the solution, and aqueous NaOH supplies Na^+ ions and OH^- ions, as shown in the following overall ionic equation.

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + 2H_2O(l)$$

Neglecting the spectator ions, the net ionic equation is as follows.

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$$

Because it is only slightly ionized, the water exists almost entirely as covalently bonded molecules. Thus, insofar as they are initially present in equal amounts, hydronium ions and hydroxide ions are almost entirely removed from the solution. The reaction effectively runs to completion because the product is only slightly ionized.

Common-Ion Effect

An equilibrium reaction may be driven in the desired direction by applying Le Châtelier's principle. Suppose hydrogen chloride gas is bubbled into a saturated solution of sodium chloride. Hydrogen chloride is extremely soluble in water, and it is almost completely ionized.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

The equilibrium for a saturated solution of sodium chloride is described by the following equation.

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

As the hydrogen chloride dissolves in sufficient quantity, it increases the concentration of Cl^- ions in the solution, which is a stress on the equilibrium system. The system can compensate, according to Le Châtelier's principle, by combining some of the added Cl^- ions with an equivalent amount of Na^+ ions. This causes some solid NaCl to precipitate out, relieving the stress of added chloride. The new equilibrium has a greater concentration of Cl^- ions but a decreased concentration of Na^+ ions. However, the product of $[Na^+]$ and $[Cl^-]$ still has the same value as before. *This phenomenon, in which the addition of an ion common to two solutes brings about precipitation or reduced ionization, is called the* **common-ion effect.**

The common-ion effect is also observed when one ion species of a weak electrolyte is added in excess to a solution. Acetic acid, CH_3COOH,

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is such an electrolyte. A 0.1 M CH_3COOH solution is only about 1.4% ionized to produce hydronium ions and acetate ions, CH_3COO^-. The ionic equilibrium is shown by the following equation.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Small additions of sodium acetate, $NaCH_3COO$ (an ionic salt that is completely dissociated in water), to a solution containing acetic acid greatly increase the acetate-ion concentration. The equilibrium shifts in the direction that uses up some of the acetate ions in accordance with Le Châtelier's principle. More molecules of acetic acid are formed and the concentration of hydronium ions is reduced. In general, the addition of a salt with an ion common to the solution of a weak electrolyte reduces the ionization of the electrolyte. Figure 18-7 shows a 0.25 M CH_3COOH solution on the left that has a pH of about 2.7. Mixing that with the 0.10 M $NaCH_3COO$ solution in the center produces the solution on the right, which has a pH of about 4.5, indicating lower $[H_3O^+]$ and thus lowered acetic acid ionization. (The universal indicator used turns red in acidic solutions, green in weakly basic solutions, and yellow in neutral solutions.)

FIGURE 18-7 The solution of CH_3COOH on the left is combined with the solution of $NaCH_3COO$ in the center. Both contain the common ion, CH_3COO^-. They produce the solution on the right, which is only slightly acidic due to the decreased ionization of the acid. The colors of the solutions are due to the addition of acid-base indicators.

SECTION REVIEW

1. Name three ways the chemical equilibrium can be disturbed.
2. Describe three situations in which ionic reactions go to completion.
3. Describe the common-ion effect.
4. Identify the common ion in each of the following situations.
   a. 5 g of NaCl is added to a 2.0 M solution of HCl
   b. 50 mL of 1.0 M $NaCH_3COO$ is added to 1.0 M CH_3COOH
   c. 10 pellets of NaOH are added to 100 mL of water
5. Predict the effect that decreasing pressure would have on each of the following reaction systems at equilibrium.
   a. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
   b. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   c. $2H_2O_2(aq) \rightleftharpoons 2H_2O(l) + O_2(g)$
   d. $3O_2(g) \rightleftharpoons 2O_3(g)$
6. When solid carbon reacts with oxygen gas to form carbon dioxide, 393.51 kJ of heat are released. Does this reaction become more favorable or less favorable as the temperature decreases? Explain.

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Equilibria of Acids, Bases, and Salts

SECTION 18-3

Objectives

- Explain the concept of acid-ionization constants, and write acid-ionization equilibrium expressions.
- Review the ionization constant of water.
- Explain buffering.
- Compare cation and anion hydrolysis.

Ionization Constant of a Weak Acid

About 1.4% of the solute molecules in a 0.1 M acetic acid solution are ionized at room temperature. The remaining 98.6% of the acetic acid molecules, CH_3COOH, remain nonionized. Thus, the solution contains three species of particles in equilibrium: CH_3COOH molecules, H_3O^+ ions, and acetate ions, CH_3COO^-. The equilibrium constant for this system expresses the equilibrium ratio of ions to molecules. From the equilibrium equation for the ionization of acetic acid, the equilibrium constant equation can be written.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

At the 0.1 M concentration, water molecules greatly exceed the number of acetic acid molecules. Without introducing a measurable error, one can assume that the molar concentration of H_2O molecules remains constant in such a solution. Thus, because both K and $[H_2O]$ are constant, the product $K[H_2O]$ is constant.

$$K[H_2O] = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

The left side of the equation can be simplified by setting $K[H_2O] = K_a$.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

The term K_a is called the **acid-ionization constant.** The acid ionization constant, K_a, like the equilibrium constant, K, is constant for a specified temperature but has a new value for each new temperature.

The acid-ionization constant for a weak acid represents a small value. To determine the numerical value of the ionization constant for acetic acid at a specific temperature, the equilibrium concentrations of H_3O^+ ions, CH_3COO^- ions, and CH_3COOH molecules must be known. The ionization of a molecule of CH_3COOH in water yields one H_3O^+ ion and one CH_3COO^- ion. These concentrations can, therefore, be found experimentally by measuring the pH of the solution.

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TABLE 18-2 Ionization of Acetic Acid

Molarity	% ionized	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.100	1.33	0.00133	0.0987	1.79×10^{-5}
0.0500	1.89	0.000945	0.0491	1.82×10^{-5}
0.0100	4.17	0.000417	0.00958	1.81×10^{-5}
0.00500	5.86	0.000293	0.00471	1.82×10^{-5}
0.00100	12.6	0.000126	0.000874	1.82×10^{-5}

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Module 8: Strong and Weakly Ionized Species, pH, and Titrations

Ionization data and constants for some dilute acetic acid solutions at 25°C are given in Table 18-2. Notice that the numerical value of K_a is almost identical for each solution molarity shown. The numerical value of K_a for CH_3COOH at 25°C can be determined by substituting numerical values for concentration into the equilibrium equation.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

At constant temperature, an increase in the concentration of CH_3COO^- ions through the addition of sodium acetate, $NaCH_3COO$, disturbs the equilibrium. This disturbance causes a decrease in $[H_3O^+]$ and an increase in $[CH_3COOH]$. Eventually, the equilibrium is reestablished with the *same* value of K_a. But there is a higher concentration of nonionized acetic acid molecules and a lower concentration of H_3O^+ ions than before the extra CH_3COO^- was added. Changes in the hydronium-ion concentration affect pH. In this example, the reduction in $[H_3O^+]$ means an increase in the pH of the solution.

(a)

(b)

FIGURE 18-8 (a) The beaker on the left contains a buffered solution and an indicator with a pH of about 7. The beaker on the right contains mostly water with a trace amount of acid and an indicator. The pH meter shows a pH of 5.00 for this solution. (b) After 5 mL of 0.10 M HCl is added to both beakers, the beaker on the left does not change color, indicating no substantial change in its pH. However, the beaker on the right undergoes a definite color change, and the pH meter shows a pH of 2.17.

Buffers

The solution just described contains both a weak acid, CH_3COOH, and a salt of the weak acid, $NaCH_3COO$. The solution can react with either an acid or a base. When small amounts of acids or bases are added, the pH of the solution remains nearly constant. The weak acid and the common ion, CH_3COO^-, act as a "buffer" against significant changes in the pH of the solution. *Because it can resist changes in pH, this solution is a* **buffered solution.** Figure 18-8 shows how a buffered and a nonbuffered solution react to the addition of an acid.

Suppose a small amount of acid is added to the acetic acid–sodium acetate solution. Acetate ions react with most of the added hydronium ions to form nonionized acetic acid molecules.

$$CH_3COO^-(aq) + H_3O^+(aq) \longrightarrow CH_3COOH(aq) + H_2O(l)$$

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The hydronium ion concentration and the pH of the solution remain practically unchanged.

Suppose a small amount of a base is added to the original solution. The OH^- ions of the base react with and remove hydronium ions to form nonionized water molecules. Acetic acid molecules then ionize and restore the equilibrium concentration of hydronium ions.

$$CH_3COOH(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3COO^-(aq)$$

The pH of the solution again remains practically unchanged.

A solution of a weak base containing a salt of the base behaves in a similar manner. The hydroxide ion concentration and the pH of the solution remain essentially constant with small additions of acids or bases. Suppose a base is added to an aqueous solution of ammonia that also contains ammonium chloride. Ammonium ions donate a proton to the added hydroxide ions to form nonionized water molecules.

$$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$$

If a small amount of an acid is added to the solution instead, hydroxide ions from the solution accept protons from the added hydronium ions to form nonionized water molecules. Ammonia molecules in the solution then ionize and restore the equilibrium concentration of hydronium ions and the pH of the solution.

$$NH_3(aq) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$$

Buffer action has many important applications in chemistry and physiology. Human blood is naturally buffered to maintain a pH of between 7.3 and 7.5. This is essential because large changes in pH would lead to serious disturbances of normal body functions. Figure 18-9 shows an example of one of the many medicines buffered to prevent large and potentially damaging changes in pH.

FIGURE 18-9 Many consumer products are buffered to protect the body from potentially harmful pH changes.

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Ionization Constant of Water

Recall from Chapter 16 that the self-ionization of water is an equilibrium reaction.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Equilibrium is established with a very low concentration of H_3O^+ and OH^- ions. The following expression for the equilibrium constant is derived from the balanced chemical equation.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

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Hydrolysis of Salts

Salts are formed during the neutralization reaction between a Brønsted acid and a Brønsted base. When a salt dissolves in water, it produces positive ions (cations) of the base from which it was formed and negative ions (anions) of the acid from which it was formed. Therefore, the solution might be expected to be neutral. The aqueous solutions of some salts, such as NaCl and KNO_3, are neutral, having a pH of 7. However, when sodium carbonate dissolves in water, the resulting solution turns red litmus paper blue, indicating a pH greater than 7. Ammonium chloride produces an aqueous solution that turns blue litmus paper red, indicating a pH less than 7. Salts formed from the combination of strong or weak acids and bases are shown in Figure 18-10.

The variation in pH values can be accounted for by examining the ions formed when each of these salts dissociates. If the ions formed are from weak acids or bases, they react chemically with the water solvent, and the pH of the solution will have a value other than 7. *A reaction between water molecules and ions of a dissolved salt is* **hydrolysis.** If the anions react with water, the process is anion hydrolysis and results in a more basic solution. If the cations react with water molecules, the process is cation hydrolysis and results in a more acidic solution.

Anion Hydrolysis

In the Brønsted sense, the anion of the salt is the conjugate base of the acid from which it was formed. It is also a proton acceptor. If the acid is weak, its conjugate base (the anion) will be strong enough to remove protons from some water molecules, proton donors, to form OH^- ions. An

(a) (b) (c) (d)

FIGURE 18-10 The universal indicator shows that the pH of salt solutions varies, depending on the strength of the acid and the base that formed the salt. (a) NaCl is formed from a strong acid and a strong base; the color of the indicator shows the pH is neutral. (b) The indicator shows the pH of the sodium acetate solution is basic. This was formed from a strong base and a weak acid. (c) The strong acid and weak base combination in ammonium chloride produces an acidic solution, as shown by the color of the indicator. (d) The weak acid and weak base that form ammonium acetate are of comparable strength. A solution of ammonium acetate is essentially neutral.

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equilibrium is established in which the net effect of the anion hydrolysis is an increase in the hydroxide-ion concentration, $[OH^-]$, of the solution.

The equilibrium equation for a typical weak acid in water, HA, forming hydronium ion and an anion, A^-, is as follows.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

From this equation, the generalized expression for K_a can be written. Recall that the concentration of water in dilute aqueous solutions is essentially constant, so it is included in the equilibrium constant instead of in the concentration ratio.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The hydrolysis reaction between water and the anion, A^-, that is produced by the dissociation of the weak acid, HA, is represented by the general equilibrium equation that follows.

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

In the forward reaction, the anion, A^-, acquires a proton from the water molecule to form the weak acid, HA, and hydroxide ion, OH^-. The extent of OH^- ion formation and the position of the equilibrium depends on the relative strength of the anion, A^-. The lower the K_a value of HA, the stronger the attraction for protons that A^- will have compared with OH^-, and the greater the production of OH^- ion will be. Therefore, as the relative strength of A^- increases, the equilibrium position lies farther to the right.

Aqueous solutions of sodium carbonate are strongly basic. The sodium ions, Na^+, in sodium carbonate do not undergo hydrolysis in aqueous solution, but the carbonate ions, CO_3^{2-}, react as a Brønsted base. A CO_3^{2-} anion acquires a proton from a water molecule to form the slightly ionized hydrogen carbonate ion, HCO_3^-, and the OH^- ion.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

The OH^- ion concentration increases until equilibrium is established. Consequently, the H_3O^+ ion concentration decreases so that the product $[H_3O^+][OH^-]$ remains equal to the ionization constant, K_w, of water at the temperature of the solution. Thus, the pH is *higher* than 7, and the solution is basic.

Cation Hydrolysis

In the Brønsted sense, the cation of the salt is the conjugate acid of the base from which it was formed. It is also a proton donor. If the base is weak, the cation is an acid strong enough to donate a proton to a water molecule, a proton acceptor, to form H_3O^+ ions. An equilibrium is established in which the net effect of the cation hydrolysis is an increase in the hydronium-ion concentration, $[H_3O^+]$, of the solution.

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The following equilibrium equation for a typical weak base, B, is used to derive the generalized expression for K_b, the base dissociation constant.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The hydrolysis reaction between water and the cation, BH^+, produced by the dissociation of the weak base, B, is represented by the general equilibrium equation that follows.

$$BH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq)$$

In the forward reaction, the cation BH^+ donates a proton to the water molecule to form the hydronium ion and the weak base, B. The extent of H_3O^+ ion formation and the position of the equilibrium depend on the relative strength of the cation, BH^+. The lower the K_b value of B, the stronger the donation of protons that BH^+ will have compared with H_3O^+, and the greater the production of H_3O^+ ions will be. Therefore, as the relative strength of BH^+ increases, the equilibrium position lies farther to the right.

Ammonium chloride, NH_4Cl, dissociates in water to produce NH_4^+ ions, Cl^- ions, and an acidic solution. Chloride ions are the conjugate base of a strong acid, HCl, so they show no noticeable tendency to hydrolyze in aqueous solution. Ammonium ions, however, are the conjugate acid of a weak base, NH_3. Ammonium ions donate protons to water molecules. Equilibrium is established with an increased $[H_3O^+]$, so the pH is *lower* than 7.

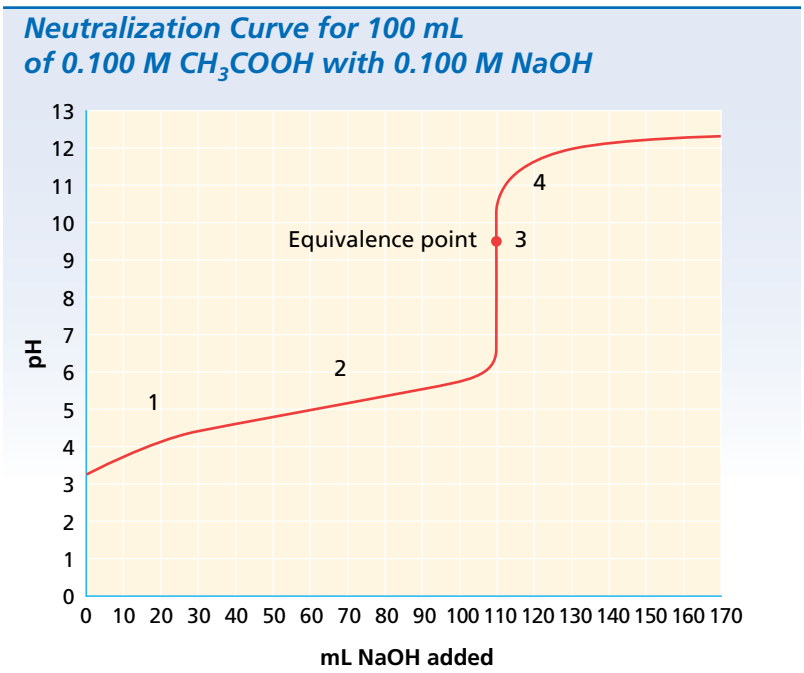

FIGURE 18-11 At point *1* on the titration curve, only acetic acid is present. The pH depends on the weak acid alone. At *2* there is a mixture of CH_3COOH and CH_3COO^-. Adding NaOH changes the pH slowly. At point *3* all acid has been converted to CH_3COO^-. This hydrolyzes to produce a slightly basic solution. At *4* the pH is due to the excess OH^- that has been added.

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Hydrolysis in Acid-Base Reactions

Hydrolysis can help explain why the end point of a neutralization reaction can occur at a pH other than 7. The hydrolysis properties of salts are determined by the relative strengths of the acids and bases from which the salts were formed. Salts can be placed in four general categories, depending on their hydrolysis properties: strong acid–strong base, strong acid–weak base, weak acid–strong base, and weak acid–weak base.

Salts of strong acids and strong bases produce neutral solutions because neither the cation of a strong base nor the anion of a strong acid hydrolyze appreciably in aqueous solutions. HCl(*aq*) is a strong acid, and NaOH(*aq*) is a strong base. Neither the Na^+ cation of the strong base nor the Cl^- anion of the strong acid undergoes hydrolysis in water solutions. Therefore, aqueous solutions of NaCl are neutral. Similarly, KNO_3 is the salt of the strong acid HNO_3 and the strong base KOH. Measurements show that the pH of an aqueous KNO_3 solution is always very close to 7.

The aqueous solutions of salts formed from reactions between weak acids and strong bases are basic, as Figure 18-11 shows. Anions of the dissolved salt are hydrolyzed in the water solvent, and the pH of the solution is raised, indicating that the hydroxide-ion concentration has increased. Aqueous solutions of sodium acetate, $NaCH_3COO$, are basic. The acetate ions, CH_3COO^-, undergo hydrolysis because they are the anions of the weak acid–acetic acid. The cations of the salt are the positive ions from a strong base, NaOH, and do not hydrolyze appreciably.

Figure 18-12 shows that salts of strong acids and weak bases produce acidic aqueous solutions. Cations of the dissolved salt are hydrolyzed in

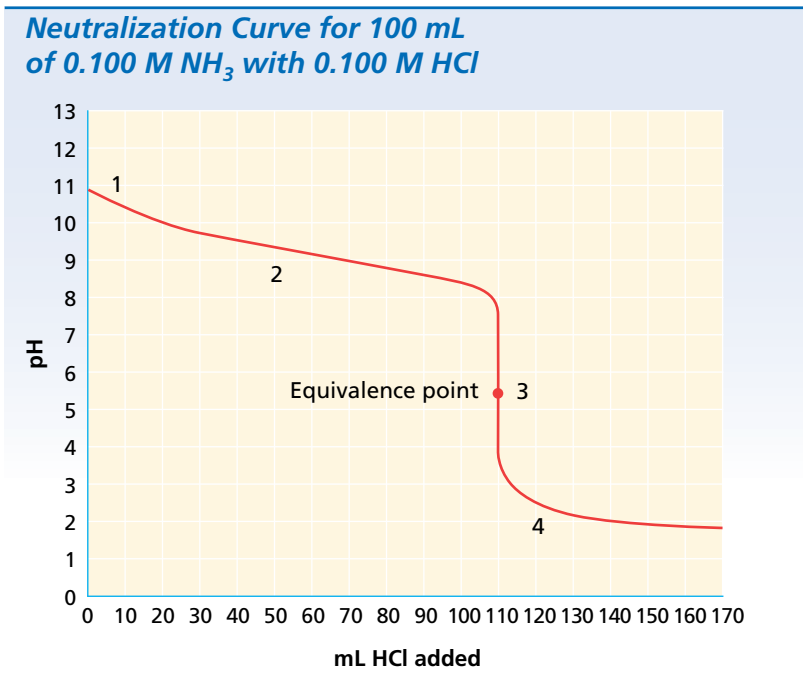

FIGURE 18-12 At point *1* on the titration curve, only aqueous ammonia is present. The pH is determined by the base alone. At *2* there is a mixture of NH_3 and NH_4^+. Adding HCl changes the pH slowly. At point *3* all aqueous ammonia has been converted to NH_4^+. At *4* the pH is determined by the excess H_3O^+ that is being added.

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the water solvent, and the pH of the solution is lowered, indicating that the hydronium-ion concentration has increased. In this case, the cations of the salt undergo hydrolysis because they are the positive ions from a weak base. The anions of the salt are the negative ions from a strong acid and do not hydrolyze appreciably. Ammonium chloride, NH_4Cl, is a salt that produces an acidic solution.

Salts of weak acids and weak bases can produce either acidic, neutral, or basic aqueous solutions, depending on the salt dissolved. This is because both ions of the dissolved salt are hydrolyzed extensively. If both ions are hydrolyzed equally, the solution remains neutral. The ions in ammonium acetate, NH_4CH_3COO, hydrolyze equally, producing a neutral solution, as shown in Figure 18-10(d) on page 572.

In cases in which both the acid and the base are very weak, the salt may undergo essentially complete decomposition to the products of hydrolysis. For example, when aluminum sulfide is placed in water, both a precipitate and a gas are formed. The reaction is symbolized by the following chemical equation.

$$Al_2S_3(s) + 6H_2O(l) \longrightarrow 2Al(OH)_3(s) + 3H_2S(g)$$

Both products are sparingly soluble in water and are removed from solution.

SECTION REVIEW

1. What is meant by an *acid-ionization constant*?
2. How is an acid-ionization equilibrium expression written?
3. What is meant by the term *buffered solution*?
4. Which of the following combinations of solutions would form buffers when they are mixed?
   a. 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaCl
   b. 25 mL of 0.5 M HNO_2 and 50 mL of 1.0 M $NaNO_2$
   c. 25 mL of 1.0 M HNO_2 and 25 mL of 1.0 M NaCl
5. What is meant by the *ion-product constant* for water? What is the value of this constant?
6. For each of the following reactions, identify each conjugate acid-base pair.
   a. $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$
   b. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
   c. $H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+$
   d. $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$
7. What is hydrolysis? Compare cation and anion hydrolysis.
8. Which of the following ions hydrolyze in aqueous solution?
   a. NO_3^- d. K^+ g. CO_3^{2-}
   b. F^- e. CH_3COO^- h. PO_4^{3-}
   c. NH_4^+ f. SO_4^{2-}
9. Identify the following solutions as acidic, basic, or neutral.
   a. 0.5 M KI c. 0.25 M NH_4NO_3
   b. 0.10 M $Ba(OH)_2$ d. 0.05 M $BaCO_3$
10. Identify the acid and base from which each of the following salts was formed.
    a. K_2CrO_4 c. CaF_2
    b. $Ca(CH_3COO)_2$ d. $(NH_4)_2SO_4$

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Solubility Equilibrium

SECTION 18-4

Objectives

- Explain what is meant by *solubility-product constants,* and calculate their values.
- Calculate solubilities using solubility-product constants.
- Carry out calculations to predict whether precipitates will form when solutions are combined.

Ionic solids dissolve in water until they are in equilibrium with their ions. An equilibrium expression can be written from the balanced chemical equation of the solid's dissociation. Concentrations of the ions can be determined from the balanced chemical equation and solubility data. The ion concentrations can then be used to determine the value of the equilibrium constant. The numerical value for the equilibrium constant can be used to predict whether precipitation occurs when solutions of various concentrations are combined.

Solubility Product

A saturated solution contains the maximum amount of solute possible at a given temperature in equilibrium with an undissolved excess of the substance. A saturated solution is not necessarily a concentrated solution. The concentration may be high or low, depending on the solubility of the solute.

A general rule is often used to express solubilities qualitatively. By this rule, a substance is said to be *soluble* if the solubility is *greater than* 1 g per 100 g of water. It is said to be *insoluble* if the solubility is *less than* 0.1 g per 100 g of water. Substances whose solubilities fall between these limits are described as *slightly soluble.*

The equilibrium principles developed in this chapter apply to all saturated solutions of sparingly soluble salts. Silver chloride is so sparingly soluble in water that it is sometimes described as insoluble. Its solution reaches saturation at a very low concentration of its ions. All Ag^+ and Cl^- ions in excess of this concentration eventually precipitate as AgCl.

Consider the equilibrium system in a saturated solution of silver chloride containing an excess of the solid salt. This system is represented by the following equilibrium equation and equilibrium-constant expression.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Because the concentration of a pure substance in the solid or liquid phase remains constant, adding more solid AgCl to this equilibrium system does not change the concentration of the undissolved AgCl present. Thus, [AgCl] does not appear in the final expression. Rearranging

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the equilibrium expression so that both constants are on the same side of the equation gives the solubility-product constant K_{sp}. *The* **solubility-product constant** *of a substance is the product of the molar concentrations of its ions in a saturated solution, each raised to the power that is the coefficient of that ion in the chemical equation.*

$$K[\mathrm{AgCl}] = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$
$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

This equation is the solubility-equilibrium expression for the reaction. It expresses the fact that the solubility-product constant, K_{sp}, of AgCl is the product of the molar concentrations of its ions in a saturated solution.

Calcium fluoride is another sparingly soluble salt. The equilibrium in a saturated CaF_2 solution is described by the following equation.

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\mathrm{F^-}(aq)$$

The solubility-product constant has the following form.

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2$$

Notice that this constant is the product of the molar concentration of Ca^{2+} ions and the molar concentration of F^- ions squared, as required by the general chemical equilibrium expression.

The numerical value of K_{sp} can be determined from solubility data. Data listed in Appendix Table A-13 (page 901) indicate that a maximum of 8.9×10^{-5} g of AgCl can dissolve in 100. g of water at 10°C. One mole of AgCl has a mass of 143.32 g. The saturation concentration, or solubility, of AgCl can therefore be expressed in moles per liter of water, which is very nearly equal to moles per liter of solution.

$$\frac{8.9 \times 10^{-5}\ \text{g AgCl}}{100.\ \text{g H}_2\text{O}} \times \frac{1\ \text{g H}_2\text{O}}{\text{mL H}_2\text{O}} \times \frac{1000\ \text{mL}}{\text{L}} \times \frac{1\ \text{mol AgCl}}{143.32\ \text{g AgCl}}$$
$$= 6.2 \times 10^{-6}\ \text{mol/L}$$

Silver chloride dissociates in solution, contributing equal numbers of Ag^+ and Cl^- ions. The ion concentrations in the saturated solution are therefore 6.2×10^{-6} mol/L.

$$[\mathrm{Ag^+}] = 6.2 \times 10^{-6}$$
$$[\mathrm{Cl^-}] = 6.2 \times 10^{-6}$$

and

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$
$$K_{sp} = (6.2 \times 10^{-6})(6.2 \times 10^{-6})$$
$$K_{sp} = (6.2 \times 10^{-6})^2$$
$$K_{sp} = 3.8 \times 10^{-11}$$

This result is the solubility-product constant of AgCl at 10°C.

From Appendix Table A-13, the solubility of CaF_2 is 1.7×10^{-3} g/100 g of water at 26°C. Expressed in moles per liter, as before, this concentra-

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tion becomes 2.2×10^{-4} mol/L. CaF_2 dissociates in solution to yield twice as many F^- ions as Ca^{2+} ions. The ion concentrations in the saturated solution are 2.2×10^{-4} for the calcium ion and $2(2.2 \times 10^{-4})$, or 4.4×10^{-4}, for the fluoride ion. Note that at equilibrium at 26°C, $[Ca^{2+}]$ equals the solubility of 2.2×10^{-4} mol/L but $[F^-]$ equals twice the solubility, or 4.4×10^{-4} mol/L. The number of moles of positive and negative ions per mole of compound must always be accounted for when using K_{sp} and solubilities.

$$K_{sp} = [Ca^{2+}][F^-]^2$$
$$K_{sp} = (2.2 \times 10^{-4})(4.4 \times 10^{-4})^2$$
$$K_{sp} = 4.3 \times 10^{-11}$$

Thus, the solubility-product constant of CaF_2 is 4.3×10^{-11} at 26°C.

It is difficult to measure very small concentrations of a solute with precision. For this reason, solubility data from different sources may report different values of K_{sp} for a substance. Thus, calculations of K_{sp} ordinarily should be limited to two significant figures. Representative values of K_{sp} at 25°C for some sparingly soluble compounds are listed in Table 18-3. Assume that all data used in K_{sp} calculations have been taken at 25°C unless otherwise specified.

At this point, you should note the difference between the solubility of a given solid and its solubility-product constant. Remember that the

TABLE 18-3 *Solubility-Product Constants, K_{sp}, at 25°C*

Salt	Ion product	K_{sp}	Salt	Ion product	K_{sp}
$AgCH_3COO$	$[Ag^+][CH_3COO^-]$	1.9×10^{-3}	CuCl	$[Cu^+][Cl^-]$	1.2×10^{-6}
AgBr	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2-}]$	6.3×10^{-36}
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	8.1×10^{-12}	FeS	$[Fe^{2+}][S^{2-}]$	6.3×10^{-18}
AgCl	$[Ag^+][Cl^-]$	1.8×10^{-10}	$Fe(OH)_2$	$[Fe^{2+}][OH^-]^2$	8.0×10^{-16}
AgI	$[Ag^+][I^-]$	8.3×10^{-17}	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	4×10^{-38}
Ag_2S	$[Ag^+]^2[S^{2-}]$	6.3×10^{-50}	HgS	$[Hg^{2+}][S^{2-}]$	1.6×10^{-52}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	1.3×10^{-33}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}]$	5.1×10^{-9}	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	1.8×10^{-11}
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	2.5×10^{-13}
CdS	$[Cd^{2+}][S^{2-}]$	8.0×10^{-27}	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	1.6×10^{-5}
$CaCO_3$	$[Ca^{2+}][CO_3^{2-}]$	2.8×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.8×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	5.3×10^{-9}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.6×10^{-8}
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	5.5×10^{-6}	PbS	$[Pb^{2+}][S^{2-}]$	8.0×10^{-28}
$CaSO_4$	$[Ca^{2+}][SO_4^{2-}]$	9.1×10^{-6}	SnS	$[Sn^{2+}][S^{2-}]$	1.0×10^{-25}
$CoCO_3$	$[Co^{2+}][CO_3^{2-}]$	1.4×10^{-13}	$SrSO_4$	$[Sr^{2+}][SO_4^{2-}]$	3.2×10^{-7}
CoS	$[Co^{2+}][S^{2-}]$	4.0×10^{-21}	ZnS	$[Zn^{2+}][S^{2-}]$	1.6×10^{-24}

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solubility-product constant is an equilibrium constant representing the product of the molar concentrations of its ions in a saturated solution. It has only one value for a given solid at a given temperature. The *solubility* of a solid is an equilibrium position that represents the amount of the solid required to form a saturated solution with a specific amount of solvent. It has an infinite number of possible values at a given temperature and is dependent on other conditions, such as the presence of a common ion.

SAMPLE PROBLEM 18-2

Calculate the solubility-product constant, K_{sp}, for copper(I) chloride, CuCl, given that the solubility of this compound at 25°C is 1.08×10^{-2} g/100. g H_2O.

SOLUTION

1 ANALYZE

Given: solubility of CuCl = 1.08×10^{-2} g CuCl/100. g H_2O

Unknown: K_{sp}

2 PLAN

Start by converting the solubility of CuCl in g/100. g H_2O to mol/L. You will need the molar mass of CuCl to get moles CuCl from grams CuCl. Then use the solubility of the $[Cu^+]$ and $[Cl^-]$ ions in the K_{sp} expression and solve for K_{sp}.

$$\frac{\text{g CuCl}}{100.\ \text{g } H_2O} \times \frac{1\ \text{g } H_2O}{1\ \text{mL } H_2O} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{1\ \text{mol CuCl}}{\text{g CuCl}} = \text{solubility in mol/L}$$

$$CuCl(s) \rightleftharpoons Cu^+(aq) + Cl^-(aq)$$

$$K_{sp} = [Cu^+][Cl^-]$$

$$[Cu^+] = [Cl^-] = \text{solubility in mol/L}$$

3 COMPUTE

The molar mass of CuCl is 99.0 g/mol.

$$\text{solubility} = \frac{1.08 \times 10^{-2}\ \cancel{\text{g CuCl}}}{100.\ \text{g } \cancel{H_2O}} \times \frac{1\ \cancel{\text{g } H_2O}}{1\ \cancel{\text{mL}}} \times \frac{1000\ \cancel{\text{mL}}}{\text{L}} \times \frac{1\ \text{mol CuCl}}{99.0\ \cancel{\text{g CuCl}}} =$$

$$1.09 \times 10^{-3}\ \text{mol/L CuCl}$$

$$[Cu^+] = [Cl^-] = 1.09 \times 10^{-3}\ \text{mol/L}$$

$$K_{sp} = (1.09 \times 10^{-3})(1.09 \times 10^{-3}) = 1.19 \times 10^{-6}$$

4 EVALUATE

The answer contains the proper number of significant figures and is close to the K_{sp} value given in Table 18-3.

PRACTICE

1. Calculate the solubility-product constant, K_{sp}, of lead(II) chloride, $PbCl_2$, which has a solubility of 1.0 g/100. g H_2O at a temperature other than 25°C.

   Answer 1.9×10^{-4}

2. Five grams of Ag_2SO_4 will dissolve in 1 L of water. Calculate the solubility product constant for this salt.

   Answer 2×10^{-5}

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Calculating Solubilities

Once known, the solubility-product constant can be used to determine the solubility of a sparingly soluble salt. Suppose you wish to know how much barium carbonate, $BaCO_3$, can be dissolved in 1 L of water at 25°C. From Table 18-3, K_{sp} for $BaCO_3$ has the numerical value 5.1×10^{-9}. The equilibrium equation is written as follows.

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$

Given the value for K_{sp}, we can write the solubility-equilibrium expression as follows.

$$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.1 \times 10^{-9}$$

Therefore, $BaCO_3$ dissolves until the product of the molar concentrations of Ba^{2+} ions and CO_3^{2-} ions equals 5.1×10^{-9}. The solubility-equilibrium equation shows that Ba^{2+} ions and CO_3^{2-} ions enter the solution in equal numbers as the salt dissolves. Thus, they have the same concentration. Let $[Ba^{2+}] = x$. Then $[CO_3^{2-}] = x$ also.

$$[Ba^{2+}][CO_3^{2-}] = K_{sp} = 5.1 \times 10^{-9}$$

$$(x)(x) = 5.1 \times 10^{-9}$$

$$x = \sqrt{5.1 \times 10^{-9}}$$

The solubility of $BaCO_3$ is 7.14×10^{-5} mol/L.

Thus, the solution concentration is 7.14×10^{-5} M for Ba^{2+} ions and 7.14×10^{-5} M for CO_3^{2-} ions.

SAMPLE PROBLEM 18-3

Calculate the solubility of silver acetate, $AgCH_3COO$, in mol/L, given the K_{sp} value for this compound listed in Table 18-3.

SOLUTION

1 ANALYZE

Given: $K_{sp} = 1.9 \times 10^{-3}$

Unknown: solubility of $AgCH_3COO$

2 PLAN

$$AgCH_3COO \rightleftharpoons Ag^+(aq) + CH_3COO^-(aq)$$

$$K_{sp} = [Ag^+][CH_3COO^-]$$

$[Ag^+] = [CH_3COO^-]$, so let $[Ag^+] = x$ and $[CH_3COO^-] = x$

3 COMPUTE

$$K_{sp} = [Ag^+][CH_3COO^-]$$

$$K_{sp} = x^2$$

$$x^2 = 1.9 \times 10^{-3}$$

$$x = \sqrt{1.9 \times 10^{-3}}$$

Solubility of $AgCH_3COO = \sqrt{1.9 \times 10^{-3}} = 4.4 \times 10^{-2}$ mol/L

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4 EVALUATE The answer has the proper number of significant figures and is close to an estimated value of 5.0×10^{-2} calculated as $\sqrt{2.5 \times 10^{-3}}$.

PRACTICE

1. Calculate the solubility of cadmium sulfide, CdS, in mol/L, given the K_{sp} value listed in Table 18-3. *Answer* 8.9×10^{-14} mol/L
2. Determine the concentration of strontium ions in a saturated solution of strontium sulfate, $SrSO_4$, if the K_{sp} for $SrSO_4$ is 3.2×10^{-7}. *Answer* 5.7×10^{-4} mol/L

Precipitation Calculations

In an earlier example, $BaCO_3$ served as the source of both Ba^{2+} and CO_3^{2-} ions. Because each mole of $BaCO_3$ yields one mole of Ba^{2+} ions and one mole of CO_3^{2-} ions, the concentrations of the two ions were equal. However, the equilibrium condition does not require that the two ion concentrations be equal. Equilibrium will still be established so that the ion product $[Ba^{2+}][CO_3^{2-}]$ does not exceed the value of K_{sp} for the system.

Similarly, if the ion product $[Ca^{2+}][F^-]^2$ is less than the value of K_{sp} at a particular temperature, the solution is unsaturated. If the ion product is greater than the value for K_{sp}, CaF_2 precipitates. This precipitation reduces the concentrations of Ca^{2+} and F^- ions until equilibrium is established.

Suppose that unequal quantities of $BaCl_2$ and Na_2CO_3 are dissolved in water and that the solutions are mixed. If the ion product $[Ba^{2+}][CO_3^{2-}]$ exceeds the K_{sp} of $BaCO_3$, a precipitate of $BaCO_3$ forms. Precipitation continues until the ion concentrations decrease to the point at which $[Ba^{2+}][CO_3^{2-}]$ equals the K_{sp}.

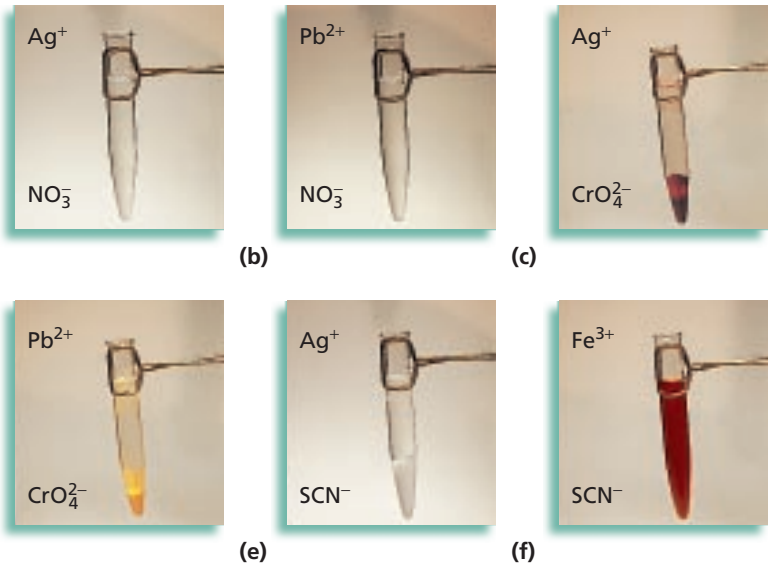

FIGURE 18-13 Nitrate salts of Ag^+ (a) and Pb^{2+} (b) are soluble. When chromate ions, CrO_4^{2-}, combine with Ag^+ (c) or Pb^{2+} (d), an insoluble salt forms. Thiocyanate ions, SCN^-, can form an insoluble salt with Ag^+ (e) or a soluble salt with Fe^{3+} (f).

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Substances differ greatly in their tendencies to form precipitates when mixed in moderate concentrations. The photos in Figure 18-13 show the behavior of some negative ions in the presence of certain metallic ions. Note that some of the combinations have produced precipitates and some have not. The solubility product can be used to predict whether a precipitate forms when two solutions are mixed.

SAMPLE PROBLEM 18-4

Will a precipitate form if 20.0 mL of 0.010 M $BaCl_2$ is mixed with 20.0 mL of 0.0050 M Na_2SO_4?

SOLUTION

1 ANALYZE

Given: concentration of $BaCl_2 = 0.010$ M
volume of $BaCl_2 = 20.0$ mL
concentration of $Na_2SO_4 = 0.0050$ M
volume of $Na_2SO_4 = 20.0$ mL

Unknown: whether a precipitate forms

2 PLAN

The two possible new pairings of ions are NaCl and $BaSO_4$. Of these, $BaSO_4$ is a sparingly soluble salt. It will precipitate if the ion product $[Ba^{2+}][SO_4^{2-}]$ in the combined solution exceeds K_{sp} for $BaSO_4$. From the list of solubility products in Table 18-3, the K_{sp} is found to be 1.1×10^{-10}. The solubility-equilibrium equation follows.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The solubility-equilibrium expression is written as follows.

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$$

First $[Ba^{2+}]$ and $[SO_4^{2-}]$ in the above solution must be found. Then the ion product is calculated and compared with the K_{sp}.

3 COMPUTE

Calculate the mole quantities of Ba^{2+} and SO_4^{2-} ions.

$$0.020 \cancel{L} \times \frac{0.010 \text{ mol } Ba^{2+}}{\cancel{L}} = 0.000\,20 \text{ mol } Ba^{2+}$$

$$0.020 \cancel{L} \times \frac{0.0050 \text{ mol } SO_4^{2-}}{\cancel{L}} = 0.000\,10 \text{ mol } SO_4^{2-}$$

Calculate the total volume of solution containing Ba^{2+} and SO_4^{2-} ions.

$$0.020 \text{ L} + 0.020 \text{ L} = 0.040 \text{ L}$$

Calculate the Ba^{2+} and SO_4^{2-} ion concentrations in the combined solution.

$$\frac{0.000\,20 \text{ mol } Ba^{2+}}{0.040 \text{ L}} = 5.0 \times 10^{-3} \text{ mol/L } Ba^{2+}$$

$$\frac{0.000\,10 \text{ mol } SO_4^{2-}}{0.040 \text{ L}} = 2.5 \times 10^{-3} \text{ mol/L } SO_4^{2-}$$

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Trial value of the ion product:

$$[Ba^{2+}][SO_4^{2-}] = (5.0 \times 10^{-3})(2.5 \times 10^{-3})$$
$$= 1.2 \times 10^{-5}$$

The ion product is much greater than the value of K_{sp}, so precipitation occurs.

4 EVALUATE

The answer contains the appropriate number of significant figures and is close to an estimated value of 1×10^{-5}, calculated as $(5 \times 10^{-3})(2 \times 10^{-3})$; because $10^{-5} > 10^{-10}$, precipitation should occur.

PRACTICE

1. Does a precipitate form when 100. mL of 0.0025 M $AgNO_3$ and 150. mL of 0.0020 M NaBr solutions are mixed?

Answer
AgBr precipitates.

2. Does a precipitate form when 20. mL of 0.038 M $Pb(NO_3)_2$ and 30. mL of 0.018 M KCl solutions are mixed?

Answer
$PbCl_2$ does *not* precipitate.

Limitations on the Use of K_{sp}

The solubility-product principle can be very useful when applied to solutions of sparingly soluble substances. It *cannot* be applied very successfully to solutions of moderately soluble or very soluble substances. This is because the positive and negative ions attract each other, and this attraction becomes appreciable when the ions are close together. Sometimes it is necessary to consider two equilibria simultaneously. For example, if either ion hydrolyzes, the salt will be more soluble than predicted when only the solubility-product constant is used. The solubility product is also sensitive to changes in solution temperature to the extent that the solubility of the dissolved substance is affected by such changes. All of these factors limit the conditions under which the solubility-product principle can be applied.

SECTION REVIEW

1. What is a solubility-product constant? How are such constants determined?
2. How are solubility-product constants used to calculate solubilities?
3. What is an ion product?
4. How are calculations to predict possible precipitation carried out?
5. What is the value of K_{sp} for Ag_2SO_4 if 5.40 g is soluble in 1.00 L of water?
6. Determine whether a precipitate will form if 20.0 mL of 1.00×10^{-7} M $AgNO_3$ is mixed with 20.0 mL of 2.00×10^{-9} M NaCl at 25°C.

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CHAPTER 18 REVIEW

CHAPTER SUMMARY

18-1

- A reaction system in which the forward and reverse reactions occur simultaneously and at the same rate is said to be in *equilibrium.* Both reactions continue, but there is no net change in the composition of the system.
- At equilibrium, the ratio of the product of the mole concentrations of substances formed to the product of the mole concentrations of reactants, each raised to the appropriate power, has a definite numerical value, K, which is the equilibrium constant at a given temperature. For values of K greater than 1, the products of the forward reaction are favored. For values of K less than 1, the products of the reverse reaction are favored.

Vocabulary

chemical equilibrium (554) chemical-equilibrium expression (556) equilibrium constant (556) reversible reaction (553)

18-2

- Any change that alters the rate of either the forward or reverse reaction disturbs the equilibrium of the system. According to Le Châtelier's principle, the equilibrium is shifted in the direction that relieves the stress.
- Catalysts increase the rates of forward and reverse reactions equally, and they do not shift an equilibrium or change the value of K.
- The common-ion effect is recognized when a solution containing ions like those of a reactant in an equilibrium system is added to the system. Le Châtelier's principle explains the response of the system to the stress.

Vocabulary

common-ion effect (567)

18-3

- The equilibrium expression for the ionization constant of the weak acid HA follows.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Salts formed from strong bases and weak acids produce aqueous solutions that are basic because of *anion hydrolysis.*
- Salts formed from strong acids and weak bases produce aqueous solutions that are acidic because of *cation hydrolysis.*
- Salts formed from strong acids and strong bases do not hydrolyze in water, and their solutions are neutral.
- Salts formed from weak acids and weak bases may produce neutral, acidic, or basic solutions, depending on the relative amounts of cation and anion hydrolysis. They may also hydrolyze completely in water solution.

Vocabulary

acid-ionization constant (569) buffered solution (570) hydrolysis (572)

18-4

- Ions of salts that are very sparingly soluble form saturated aqueous solutions at low concentrations. The solubility-equilibrium expression for such salts yields a useful constant—the solubility-product constant, K_{sp}. The value of K_{sp} equals the product of the molar concentrations of solute ions in the saturated solution raised to a power equal to the coefficient in the balanced equation for the solution of one mole.

Vocabulary

solubility-product constant (578)

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REVIEWING CONCEPTS

1. Describe and explain how the concentrations of A, B, C, and D change from the time when A and B are first combined to the point at which equilibrium is established for the reaction $A + B \rightleftharpoons C + D$. (18-1)

2. a. Write the general expression for an equilibrium constant based on the equation $nA + mB + \ldots \rightleftharpoons xC + yD + \ldots$

b. What information is provided by the value of K for a given equilibrium system at a specified temperature? (18-1)

3. In general, which reaction is favored (forward, reverse, or neither) if the value of K at a specified temperature is

a. equal to 1?

b. very small?

c. very large? (18-1)

4. Predict whether each of the following pressure changes would favor the forward or reverse reaction.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

a. increased pressure

b. decreased pressure (18-2)

5. In heterogeneous reaction systems, what types of substances do not appear in the equilibrium constant expression? Why? (18-2)

6. Explain the effect of a catalyst on an equilibrium system. (18-2)

7. Predict the effect of each of the following on the indicated equilibrium system in terms of which reaction will be favored (forward, reverse, or neither).

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + 184\ kJ$$

a. addition of Cl_2

b. removal of HCl

c. increased pressure

d. decreased temperature

e. removal of H_2

f. decreased pressure

g. addition of a catalyst

h. increased temperature

i. decreased system volume (18-2)

8. How would parts (a) through (i) of item 7 affect the new equilibrium concentration of HCl and the value of K at the new equilibrium? (18-2)

9. Changes in the concentrations of the reactants and products at equilibrium have no impact on the value of the equilibrium constant. Explain. (18-2)

10. What relative pressure (high or low) would result in the production of the maximum level of CO_2 according to the following? Explain. (18-2)

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

11. What relative conditions (reactant concentrations, pressure, and temperature) would favor a high equilibrium concentration of the underlined substance in each of the following equilibrium systems?

a. $2CO(g) + O_2(g) \rightleftharpoons \underline{2CO_2(g)} + 167\ kJ$

b. $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underline{Cu(NH_3)_4^{2+}(aq)} + 42\ kJ$

c. $2HI(g) + 12.6\ kJ \rightleftharpoons H_2(g) + \underline{I_2(g)}$

d. $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + \underline{2Cl_2(g)} + 113\ kJ$

e. $H_2O(l) + 42\ kJ \rightleftharpoons \underline{H_2O(g)}$ (18-2)

12. A combustion reaction proceeding in air under standard pressure is transferred to an atmosphere of pure oxygen under the same pressure.

a. What effect would you observe?

b. How can you account for this effect? (18-2)

13. What two factors determine the extent to which reacting ions are removed from solution? (18-2)

14. Identify the three conditions under which ionic reactions can run to completion, and write an equation for each. (18-2)

15. a. Write the ion-product constant expression for water.

b. What is the value of this constant at 25°C? (18-3)

16. List and distinguish between the four general categories of salts, based on their hydrolysis properties, and give an example of each. (18-3)

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17. The pH of a solution containing both acetic acid and sodium acetate is higher than that of a solution containing the same concentration of acetic acid alone. Explain. (18-3)

18. The ionization constant, K_a, for acetic acid is 1.8×10^{-5} at 25°C. Explain the significance of this value. (18-3)

19. a. From the development of K_a described in Section 18-3, show how you would express an ionization constant, K_b, for the weak base NH_3.
b. In this case, $K_b = 1.8 \times 10^{-5}$. What is the significance of this numerical value to equilibrium? (18-3)

20. A saturated solution is not necessarily a concentrated solution. Explain. (18-4)

21. What rule of thumb is used to distinguish between soluble, insoluble, and slightly soluble substances? (18-4)

22. What is the major solubility characteristic of those types of substances typically involved in solubility-equilibrium systems? (18-4)

23. What is the relationship between K_{sp} and the product of the ion concentrations in terms of determining whether a solution of those ions is saturated? (18-4)

PROBLEMS

Equilibrium Constant

24. Determine the value of the equilibrium constant for each reaction given, assuming that the equilibrium concentrations are found to be those specified. (Concentrations are in mol/L.) (Hint: See Sample Problem 18-1.)
a. $A + B \rightleftharpoons C$; [A] = 2.0; [B] = 3.0; [C] = 4.0
b. $D + 2E \rightleftharpoons F + 3G$; [D] = 1.5; [E] = 2.0; [F] = 1.8; [G] = 1.2
c. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $[N_2] = 0.45$; $[H_2] = 0.14$; $[NH_3] = 0.62$

25. An equilibrium mixture at a specific temperature is found to consist of 1.2×10^{-3} mol/L HCl, 3.8×10^{-4} mol/L O_2, 5.8×10^{-2} mol/L H_2O, and 5.8×10^{-2} mol/L Cl_2 according to the following: $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$. Determine the value of the equilibrium constant for this system.

26. At 450°C the value of the equilibrium constant for the following system is 6.59×10^{-3}. If $[NH_3] = 1.23 \times 10^{-4}$ M and $[H_2] = 2.75 \times 10^{-3}$ M at equilibrium, determine the concentration of N_2 at that point.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

27. The value of the equilibrium constant for the reaction below is 40.0 at a specified temperature. What would be the value of that constant for the reverse reaction under the same conditions? $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Solubility-Product Constant

28. The ionic substance EJ dissociates to form E^{2+} and J^{2-} ions. The solubility of EJ is 8.45×10^{-6} mol/L. What is the value of the solubility-product constant? (Hint: See Sample Problem 18-2.)

29. Calculate the solubility-product constant K_{sp} for each of the following, based on the solubility information provided:
a. $BaSO_4 = 2.4 \times 10^{-4}$ g/100. g H_2O at 20°C
b. $Ca(OH)_2 = 0.173$ g/100. g H_2O at 20°C

30. Calculate the solubility of a substance MN that ionizes to form M^{2+} and N^{2-} ions, given that $K_{sp} = 8.1 \times 10^{-6}$. (Hint: See Sample Problem 18-3.)

31. Use the K_{sp} values given in Table 18-3 to evaluate the solubility of each of the following in moles per liter.
a. AgBr
b. CoS

32. Complete each of the following relative to the reaction that occurs when 25.0 mL of 0.0500 M $Pb(NO_3)_2$ is combined with 25.0 mL of 0.0400 M Na_2SO_4 if equilibrium is reached at 25°C.
a. Write the solubility-equilibrium equation at 25°C.
b. Write the solubility-equilibrium expression for the net reaction.

33. The ionic substance T_3U_2 ionizes to form T^{2+} and U^{3-} ions. The solubility of T_3U_2 is 3.77×10^{-20} mol/L. What is the value of the solubility-product constant?

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34. A solution of AgI contains 2.7×10^{-10} mol/L Ag^+. What is the maximum I^- concentration that can exist in this solution?

35. Calculate whether a precipitate will form if 0.35 L of 0.0044 M $Ca(NO_3)_2$ and 0.17 L of 0.000 39 M NaOH are mixed at 25°C. (See Table 18-3 for K_{sp} values.) (Hint: See Sample Problem 18-4.)

36. Determine whether a precipitate will form if 1.70 g of solid $AgNO_3$ and 14.5 g of solid NaCl are dissolved in 200. mL of water to form a solution at 25°C.

37. If 2.50 g of solid $Fe(NO_3)_3$ is added to 100. mL of a 1.0×10^{-20} M NaOH solution, will a precipitate form?

MIXED REVIEW

38. Calcium carbonate is only slightly soluble in water.

a. Write the equilibrium equation for calcium carbonate in solution.

b. Write the equilibrium-constant expression, K, and the solubility-product constant expression, K_{sp}, for the equilibrium in a saturated solution of $CaCO_3$.

39. Calculate the concentration of Hg^{2+} ions in a saturated solution of $HgS(s)$. What volume of solution contains one Hg^{2+} ion?

40. Calculate the equilibrium constant, K, for the following reaction at 900°C.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

The components were analyzed and it was found that $[H_2] = 0.61$ mol/L, $[CO_2] = 1.6$ mol/L, $[H_2O] = 1.1$ mol/L, and $[CO] = 1.4$ mol/L.

41. A solution in equilibrium with solid barium phosphate is found to have a barium ion concentration of 5×10^{-4} M and a K_{sp} of 3.4×10^{-23}. Calculate the concentration of phosphate ion.

42. At 25°C, the value of K is 1.7×10^{-13} for the following reaction.

$$N_2O(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons 2NO(g)$$

It is determined that $[N_2O] = 0.0035$ mol/L and $[O_2] = 0.0027$ mol/L. Using this information, what is the concentration of $NO(g)$ at equilibrium?

43. Tooth enamel is composed of the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, which has a K_{sp} of 6.8×10^{-37}. The molar solubility of hydroxyapatite is 2.7×10^{-5} mol/L. When hydroxyapatite is reacted with fluoride, the OH^- is replaced with the F^- ion on the mineral, forming fluorapatite, $Ca_5(PO_4)_3F$. (The latter is harder and less susceptible to caries.) The K_{sp} of fluorapatite is 1×10^{-60}. Calculate the solubility of fluorapatite in water. Given your calculations, can you support the fluoridation of drinking water?

44. Determine if a precipitate will form when 0.96 g Na_2CO_3 is combined with 0.20 g $BaBr_2$ in a 10 L solution ($K_{sp} = 2.8 \times 10^{-9}$).

45. For the formation of ammonia, the equilibrium constant is calculated to be 5.2×10^{-5} at 25°C. After analysis, it is determined that $[N_2] = 2.00$ M and $[H_2] = 0.80$ M. How many grams of ammonia are in the 10 L reaction vessel at equilibrium? Use the following equilibrium equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

CRITICAL THINKING

46. Predicting Outcomes When gasoline burns in an automobile engine, nitric oxide is formed from oxygen and nitrogen. Nitric oxide is a major air pollutant. High temperatures like those found in a combustion engine are needed for the reaction. The reaction follows.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

K for the reaction is 0.01 at 2000°C. If 4.0 mol of N_2, 0.1 mol of O_2, and 0.08 mol of NO are placed in a 1.0 L vessel at 2000°C, predict which reaction will be favored.

TECHNOLOGY & LEARNING

47. Graphing Calculator Calculating the Equilibrium Constant, K, for a System

The graphing calculator can run a program that calculates K for a system, given the concentrations of the products and the concentrations of the reactants.

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Given the balanced chemical equation

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

and the equilibrium mixture at 425°C, you can calculate the equilibrium constant for the system. Then you can use the program to make calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. What is the equilibrium constant given the following equilibrium concentrations? 0.012840 mol/L of H_2, 0.006437 mol/L of I_2, and 0.066807 mol/L of HI
b. What is the equilibrium constant given the following equilibrium concentrations? 0.000105 mol/L of H_2, 0.000107 mol/L of I_2, and 0.000779 mol/L of HI
c. What is the equilibrium constant given the following equilibrium concentrations? 0.000527 mol/L of H_2, 0.000496 mol/L of I_2, and 0.003757 mol/L of HI

HANDBOOK SEARCH

48. An equilibrium system helps maintain the pH of the blood. Review the material on the carbon dioxide–bicarbonate ion equilibrium system in Group 14 of the *Elements Handbook* and answer the following.
a. Write the equation for the equilibrium system that responds to changes in H_3O^+ concentration.
b. Use Le Châtelier's principle to explain how hyperventilation affects this system.
c. How does this system maintain pH when acid is added?

49. The reactions used to confirm the presence of transition metal ions often involve the formation of precipitates. Review the analytical tests for the transition metals in the *Elements Handbook*. Use that information and Table 18-3 to determine the minimum concentration of Zn^{2+} needed to produce a precipitate that confirms the presence of Zn. Assume enough sulfide ion reagent is added to the unknown solution in the test tube to produce a sulfide ion concentration of 1.4×10^{-20} M.

RESEARCH & WRITING

50. Find photos of several examples of stalagmites and stalactites in various caves. Investigate the equilibrium processes involved in the formation of stalagmites and stalactites.

51. Carry out library research on the use of catalysts in industrial processes. Explain what types of catalysts are used for specific processes, such as the Haber process.

ALTERNATIVE ASSESSMENT

52. Performance Fill a drinking glass with water and add sugar by the teaspoonful, stirring after each addition. Continue adding the sugar until some of the sugar remains undissolved, even after vigorous stirring. Now heat the sugar-water solution. How are you using Le Châtelier's principle to shift the equilibrium of the system?

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CHAPTER 19

Oxidation-Reduction Reactions

Oxidation-reduction reactions propel rockets into space.

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Oxidation and Reduction

SECTION 19-1

OBJECTIVES

- Assign oxidation numbers to reactant and product species.
- Define *oxidation* and *reduction*.
- Explain what an oxidation-reduction reaction (redox reaction) is.

Oxidation-reduction reactions involve a transfer of electrons. Oxidation involves the loss of electrons, whereas reduction involves the gain of electrons. Reduction and oxidation half-reactions must occur simultaneously. These processes can be identified through the understanding and use of oxidation numbers (oxidation states).

Oxidation States

Oxidation states were defined in Chapter 7. The oxidation number assigned to an element in a molecule is based on the distribution of electrons in that molecule. The rules by which oxidation numbers are assigned were given in Chapter 7. These rules are summarized in Table 19-1.

TABLE 19-1 *Rules for Assigning Oxidation Numbers*

Rule	Example
1. The oxidation number of any uncombined element is 0.	The oxidation number of Na(*s*) is 0.
2. The oxidation number of a monatomic ion equals the charge on the ion.	The oxidation number of Cl^- is –1.
3. The more electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.	The oxidation number of O in NO is –2.
4. The oxidation number of fluorine in a compound is always –1.	The oxidation number of F in LiF is –1.
5. Oxygen has an oxidation number of –2 unless it is combined with F, when it is +2, or it is in a peroxide, such as H_2O_2, when it is –1.	The oxidation number of O in NO_2 is –2.
6. The oxidation state of hydrogen in most of its compounds is +1 unless it is combined with a metal, in which case it is –1.	The oxidation number of H in LiH is –1.
7. In compounds, Group 1 and 2 elements and aluminum have oxidation numbers of +1, +2, and +3, respectively.	The oxidation number of Ca in $CaCO_3$ is +2.
8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.	The oxidation number of C in $CaCO_3$ is +4.
9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.	The oxidation number of P in $H_2PO_4^-$ is +5.

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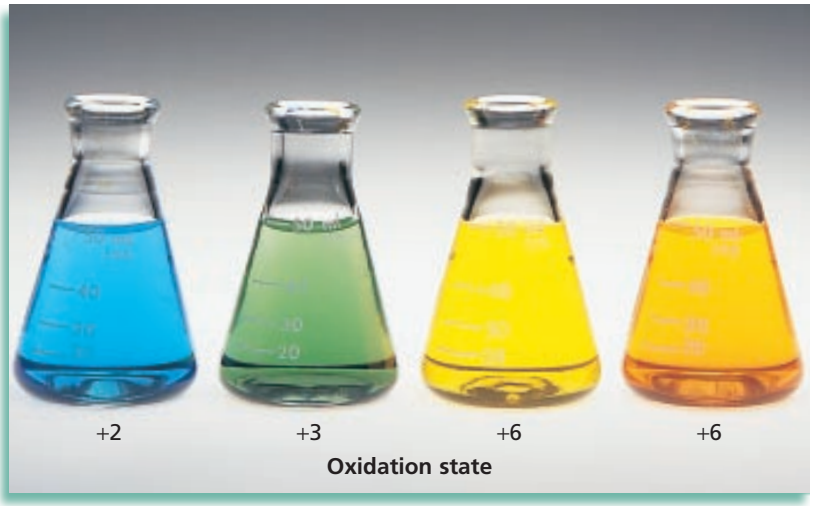

FIGURE 19-1 The color of solutions containing chromium compounds changes with the oxidation state of chromium.

Chromium provides a very visual example of different oxidation numbers. Different oxidation states of chromium have dramatically different colors, as can be seen in Figure 19-1. The chromium(II) chloride solution is blue, chromium(III) chloride solution is green, potassium chromate solution is yellow, and potassium dichromate solution is orange.

Oxidation

FIGURE 19-2 Sodium and chlorine react violently to form NaCl. The synthesis of NaCl from its elements illustrates the oxidation-reduction process.

Reactions in which the atoms or ions of an element experience an increase in oxidation state are **oxidation** *processes.* The combustion of metallic sodium in an atmosphere of chlorine gas is shown in Figure 19-2. The sodium ions and chloride ions produced during this strongly exothermic reaction form a cubic crystal lattice in which sodium cations are ionically bonded to chloride anions. The chemical equation for this reaction is written as follows.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

The formation of sodium ions illustrates an oxidation process because each sodium atom loses an electron to become a sodium ion. The oxidation state is represented by placing an oxidation number above the symbol of the atom and the ion.

$$\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$$

The oxidation state of sodium has changed from 0, its elemental state, to the +1 state of the ion (Rules 1 and 7, Table 19-1). *A species whose oxidation number increases is* **oxidized.** The sodium atom is *oxidized* to a sodium ion.

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Reduction

Reactions in which the oxidation state of an element decreases are **reduction** *processes.* Consider the behavior of chlorine in its reaction with sodium. Each chlorine atom accepts an electron and becomes a chloride ion. The oxidation state of chlorine decreases from 0 to –1 for the chloride ion (Rules 1 and 2, Table 19-1).

$$\overset{0}{Cl_2} + 2e^- \longrightarrow \overset{-1}{2Cl^-}$$

A species that undergoes a decrease in oxidation state is **reduced.** The chlorine atom is reduced to the chloride ion.

Oxidation and Reduction as a Process

Electrons are produced in oxidation and acquired in reduction. Therefore, for oxidation to occur during a chemical reaction, reduction must occur simultaneously. Furthermore, the number of electrons produced in oxidation must equal the number of electrons acquired in reduction. This makes sense when you recall that electrons are negatively charged and that for charge to be conserved, the number of electrons lost must equal the number of electrons gained. You learned in Chapter 8 that mass is conserved in any chemical reaction. Therefore, the masses of the elements that undergo oxidation and reduction and the electrons that are exchanged are conserved.

A transfer of electrons causes changes in the oxidation states of one or more elements. *Any chemical process in which elements undergo changes in oxidation number is an* **oxidation-reduction reaction.** This name is often shortened to **redox reaction.** An example of a redox reaction can be seen in Figure 19-3, in which copper is being oxidized and NO_3^- from nitric acid is being reduced. *The part of the reaction involving oxidation or reduction alone can be written as a* **half-reaction.** The overall equation for a redox reaction is the sum of two half-reactions. Because the number of electrons involved is the same for oxidation and reduction, they cancel each other out and do not appear in the overall chemical equation. Equations for the reaction between nitric acid and copper illustrate the relationship between half-reactions and the overall redox reaction.

$$\overset{0}{3Cu} \longrightarrow \overset{+2}{3Cu^{2+}} + 6e^- \qquad \text{(oxidation half-reaction)}$$

$$\overset{+5\ -2}{2NO_3^-} + 6e^- + \overset{+1}{8H^+} \longrightarrow \overset{+2\ -2}{2NO} + \overset{+1\ -2}{4H_2O} \qquad \text{(reduction half-reaction)}$$

$$\overset{0}{3Cu} + \overset{+5}{2NO_3^-} + 8H^+ \longrightarrow \overset{+2}{3Cu^{2+}} + \overset{+2}{2NO} + 4H_2O \qquad \text{(redox reaction)}$$

Notice that electrons lost in oxidation appear on the product side of the oxidation half-reaction. Electrons are gained in reduction and

FIGURE 19-3 Copper is oxidized and nitrogen monoxide is produced when this penny is placed in a nitric acid solution.

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appear as reactants in the reduction half-reaction. When metallic copper reacts in nitric acid, three copper atoms are oxidized to Cu^{2+} ions as two nitrogen atoms are reduced from a +5 oxidation state to a +2 oxidation state. Atoms are conserved. This is illustrated by the balanced chemical equation for the reaction between copper and nitric acid.

If none of the atoms in a reaction change oxidation state, the reaction is *not* a redox reaction. For example, sulfur dioxide gas, SO_2, dissolves in water to form an acidic solution containing a low concentration of sulfur*ous* acid, H_2SO_3.

$$\overset{+4\ -2}{SO_2} + \overset{+1\ -2}{H_2O} \longrightarrow \overset{+1\ +4\ -2}{H_2SO_3}$$

The oxidation states of all elemental species remain unchanged in this composition reaction. Therefore, it is *not* a redox reaction.

When a solution of sodium chloride is added to a solution of silver nitrate, an ion-exchange reaction occurs and white silver chloride precipitates.

$$\overset{+1}{Na^+} + \overset{-1}{Cl^-} + \overset{+1}{Ag^+} + \overset{+5\ -2}{NO_3^-} \longrightarrow \overset{+1}{Na^+} + \overset{+5\ -2}{NO_3^-} + \overset{+1\ -1}{AgCl}$$

The oxidation state of each monatomic ion remains unchanged. Again, this reaction is not an oxidation-reduction reaction.

Redox Reactions and Covalent Bonds

Both the synthesis of NaCl from its elements and the reaction between copper and nitric acid involve ionic bonding. Substances with covalent bonds also undergo redox reactions. An oxidation number, unlike an ionic charge, has no physical meaning. That is, the oxidation number assigned to a particular atom is based on its electronegativity relative to the other atoms to which it is bonded in a given molecule; it is not based on any real charge on the atom. For example, an ionic charge of 1– results from the complete gain of one electron by an atom or other neutral species, whereas an oxidation state of –1 means an increased attraction for a bonding electron. A change in oxidation number does not require a change in actual charge.

When hydrogen burns in chlorine, a covalent bond forms from the sharing of two electrons. The two bonding electrons in the hydrogen chloride molecule are not shared equally. Rather, the pair of electrons is more strongly attracted to the chlorine atom because of its higher electronegativity.

$$\overset{0}{H_2} + \overset{0}{Cl_2} \longrightarrow \overset{+1\ -1}{2HCl}$$

As specified by Rule 3 in Table 19-1, chlorine in HCl is assigned an oxidation number of –1. Thus, the oxidation number for the chlorine atoms changes from 0, its oxidation number in the elemental state, to –1; chlorine atoms are reduced. As specified by Rule 1, the oxidation number of each hydrogen atom in the hydrogen molecule is 0. As specified by Rule 6, the oxidation state of the hydrogen atom in the HCl molecule is +1;

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the hydrogen atom is oxidized. No electrons have been totally lost or gained by either atom. Hydrogen has donated a share of its bonding electron to the chlorine; it has not completely transferred that electron. The assignment of oxidation numbers allows the determination of the partial transfer of electrons in compounds that are not ionic. Thus, increases or decreases in oxidation number can be seen in terms of complete or partial loss or gain of electrons.

Reactants and products in redox reactions are not limited to monatomic ions and uncombined elements. Elements in molecular compounds or polyatomic ions can also be oxidized and reduced if they have more than one non-zero oxidation state. An example of this is provided in the reaction between the copper penny and nitric acid when the nitrate ion, NO_3^-, is converted to nitrogen monoxide, NO. Nitrogen is reduced in this reaction. Usually we refer to the oxidation or reduction of the entire molecule or ion. Instead of saying the nitrogen atom is reduced, we say the nitrate ion is reduced to nitrogen monoxide.

$$\cdots + \overset{+5}{NO_3^-} \longrightarrow \overset{+2}{NO} + \cdots$$

SECTION REVIEW

1. How are oxidation numbers assigned?

2. Label each of the following half-reactions as either an oxidation or a reduction half-reaction:

a. $\overset{0}{Br_2} + 2e^- \longrightarrow 2\overset{-1}{Br^-}$

b. $\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$

c. $2\overset{-1}{Cl^-} \longrightarrow \overset{0}{Cl_2} + 2e^-$

d. $\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$

e. $\overset{+1}{Na^+} + e^- \longrightarrow \overset{0}{Na}$

f. $\overset{0}{Fe} \longrightarrow \overset{+2}{Fe^{2+}} + 2e^-$

g. $\overset{+2}{Cu^{2+}} + 2e^- \longrightarrow \overset{0}{Cu}$

h. $\overset{+3}{Fe^{3+}} + e^- \longrightarrow \overset{+2}{Fe^{2+}}$

3. Which of the following equations represent redox reactions?

a. $2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$

b. $H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(l)$

c. $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

d. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

e. $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$

4. For each redox equation identified in the previous question, determine which element is oxidized and which is reduced.

5. Use the equations below for the redox reaction between aluminum metal and sodium metal to answer the following.

$$3\overset{0}{Na} \longrightarrow 3\overset{+1}{Na^+} + 3e^- \qquad \text{(oxidation)}$$

$$\overset{+3}{Al^{3+}} + 3e^- \longrightarrow \overset{0}{Al} \qquad \text{(reduction)}$$

$$3\overset{0}{Na} + \overset{+3}{Al^{3+}} \longrightarrow 3\overset{+1}{Na^+} + \overset{0}{Al} \qquad \text{(redox reaction)}$$

a. Explain how this reaction illustrates that charge is conserved in a redox reaction.

b. Explain how this reaction illustrates that mass is conserved in a redox reaction.

c. Explain why electrons do not appear as reactants or products in the combined equation.

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Skunk-Spray Remedy

So that pretty black cat with the white stripe down its back wasn't a cat after all? Well, hold off on dumping Fido into a tomato-juice bath. Chemistry has a much better way of conquering skunk spray.

Paul Krebaum, the inventor of a new deskunking formula, says that while working as a materials engineer, he constantly had to deal with the less-than-pleasant smell of the hydrogen sulfide gas that was released from one of his experiments. Mr. Krebaum was losing popularity with his neighbors, and venting off the gas only partially solved the problem. A better solution, he decided, would be to find a way to eliminate the smell entirely.

Mr. Krebaum rifled through his old chemistry books and found that hydrogen peroxide could oxidize these sulfur-containing compounds to much less smelly components. He immediately whipped up a hydrogen peroxide mixture, and it worked like a charm.

The reaction by which the hydrogen sulfide was destroyed, producing sulfate compounds that do not have the unpleasant odor, can be seen in the following equation.

$$2NaOH + 4H_2O_2 + H_2S \longrightarrow Na_2SO_4 + 6H_2O$$

"The receptors that are in your nose are sensitive to sulfur in its low oxidation state," says Mr. Krebaum. "However, they are not sensitive to sulfur in its high oxidation state."

Skunk spray gets its odor from chemicals called mercaptans.

Some time later, a friend of Mr. Krebaum's complained to him that a skunk had sprayed his pet. Because the odor in a skunk's spray also comes from compounds containing sulfur in a low oxidation state, Mr. Krebaum thought his solution might also work on this age-old problem. He mixed up a milder version to try out on the pet: 1 quart 3% hydrogen peroxide solution, 1/4 cup baking soda, and 1 teaspoon liquid soap. His friend tried it out, and the result was one wet and unhappy—but much less smelly—pet.

Mr. Krebaum says that the hydrogen peroxide in the remedy actually oxidizes the compounds, while the baking soda reduces the acidity of the mixture and the soap helps to wash out the greasy skunk spray. The reaction that occurs can be seen in the following equation. The symbol *R* represents all the other elements in the sulfur-containing compound found in skunk spray.

$$RSH + 3H_2O_2 + NaHCO_3 \longrightarrow RSO_3Na + 4H_2O + CO_2$$

The pet should be washed thoroughly with the mixture, taking care to avoid its eyes. If the mixture is left on for a few minutes—long enough for the reaction to occur—and then rinsed away with tap water, the smell will disappear.

The formula does not bleach or have any other negative side effects. Mr. Krebaum does have one warning: mix the formula just before using it because the mixture breaks down quickly. The reaction releases oxygen, so the formula should not be put into a sealed container; it will build up pressure and could eventually blow the top. For these reasons, bottles of "Krebaum's Skunkinator" will not be appearing on drug-store shelves any time soon.

How did Paul Krebaum's research into the properties of H_2S result in a benefit to dog owners?

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Balancing Redox Equations

SECTION 19-2

OBJECTIVES

- Explain what must be conserved in redox equations.
- Balance redox equations by using the half-reaction method.

Equations for simple redox reactions can be balanced by inspection, which you learned to do in Chapter 8. Most redox equations, however, require more systematic methods. The equation-balancing process requires the use of oxidation numbers. In a balanced equation, both charge and mass are conserved. Although oxidation and reduction half-reactions occur together, their reaction equations are balanced separately, then combined to give the balanced redox-reaction equation.

Half-Reaction Method

The *half-reaction method,* or ion-electron method, for balancing redox equations consists of seven steps. Oxidation numbers are assigned to all atoms and polyatomic ions to determine which species are part of the redox process. The oxidation and reduction equations are balanced separately for mass and charge. They are then added together to produce a complete balanced equation. These seven steps are applied to balance the reaction of hydrogen sulfide and nitric acid. Sulfuric acid, nitrogen dioxide, and water are the products of the reaction.

1. ***Write the formula equation if it is not given in the problem. Then write the ionic equation.***

Formula equation: $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Ionic equation: $H_2S + H^+ + NO_3^- \longrightarrow 2H^+ + SO_4^{2-} + NO_2 + H_2O$

2. ***Assign oxidation numbers. Delete substances containing only elements that do not change oxidation state.***

$$\overset{+1\ -2}{H_2S} + \overset{+1}{H^+} + \overset{+5\ -2}{NO_3^-} \longrightarrow 2\overset{+1}{H^+} + \overset{+6\ -2}{SO_4^{2-}} + \overset{+4\ -2}{NO_2} + \overset{+1\ -2}{H_2O}$$

The sulfur changes oxidation state from –2 to +6. The nitrogen changes oxidation state from +5 to +4. The other substances are deleted.

$$\overset{+1\ -2}{H_2S} + \overset{+5\ -2}{NO_3^-} \longrightarrow \overset{+6\ -2}{SO_4^{2-}} + \overset{+4\ -2}{NO_2}$$

The remaining species are used in step 3.

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3. ***Write the half-reaction for oxidation.*** In this example, the sulfur is being oxidized.

$$\overset{-2}{H_2S} \longrightarrow \overset{+6}{SO_4^{2-}}$$

- ***Balance the atoms.*** To balance the oxygen in this half-reaction, H_2O must be added to the left side. This gives 10 extra hydrogen atoms on that side of the equation. Therefore, 10 hydrogen ions are added to the right side. In basic solution, OH^- ions and water may be used to balance atoms.

$$\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+$$

- ***Balance the charge.*** Electrons are added to the side having the greater positive net charge. The left side of the equation has no net charge; the right side has a net charge of 8+. For the charges to balance, each side must have the same net charge. Therefore, 8 electrons are added to the product side so that it has no charge and balances with the reactant side of the equation. Notice that the oxidation of sulfur from a state of –2 to +6 indicates a loss of 8 electrons.

$$\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-$$

The oxidation half-reaction is now balanced.

4. ***Write the half-reaction for reduction.*** In this example, nitrogen is being reduced from a +5 state to a +4 state.

$$\overset{+5}{NO_3^-} \longrightarrow \overset{+4}{NO_2}$$

- ***Balance the atoms.*** H_2O must be added to the product side of the reaction to balance the oxygen atoms. Therefore, two hydrogen ions must be added to the reactant side to balance the hydrogen atoms.

$$\overset{+5}{NO_3^-} + 2H^+ \longrightarrow \overset{+4}{NO_2} + H_2O$$

- ***Balance the charge.*** Electrons are added to the side having the greater positive net charge. The left side of the equation has a net charge of 1+. Therefore, 1 electron must be added to this side to balance the charge.

$$\overset{+5}{NO_3^-} + 2H^+ + e^- \longrightarrow \overset{+4}{NO_2} + H_2O$$

The reduction half-reaction is now balanced.

5. ***Conserve charge by adjusting the coefficients in front of the electrons so that the number lost in oxidation equals the number gained in reduction.*** Write the ratio of the number of electrons lost to the number of electrons gained.

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{8}{1}$$

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This ratio is already in its lowest terms. If it were not, it would need to be reduced. Multiply the oxidation half-reaction by 1 (it remains unchanged) and the reduction half-reaction by 8. The number of electrons lost now equals the number of electrons gained.

$$1\left(\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-\right)$$

$$8\left(\overset{+5}{NO_3^-} + 2H^+ + e^- \longrightarrow \overset{+4}{NO_2} + H_2O\right)$$

6. ***Combine the half-reactions, and cancel out anything common to both sides of the equation.***

$$\overset{-2}{H_2S} + 4H_2O \longrightarrow \overset{+6}{SO_4^{2-}} + 10H^+ + 8e^-$$

$$\overset{+5}{8NO_3^-} + 16H^+ + 8e^- \longrightarrow \overset{+4}{8NO_2} + 8H_2O$$

$$\overset{+5}{8NO_3^-} + \cancel{16}^{\,6}\cancel{H^+} + \cancel{8e^-} + \overset{-2}{H_2S} + \cancel{4H_2O} \longrightarrow$$

$$\overset{+4}{8NO_2} + \cancel{8}^{\,4}\cancel{H_2O} + \overset{+6}{SO_4^{2-}} + \cancel{10H^+} + \cancel{8e^-}$$

Each side of the above equation has $10H^+$, $8e^-$, and $4H_2O$. These cancel each other out and do not appear in the balanced equation.

$$\overset{+5}{8NO_3^-} + \overset{-2}{H_2S} + 6H^+ \longrightarrow \overset{+4}{8NO_2} + 4H_2O + \overset{+6}{SO_4^{2-}}$$

7. ***Combine ions to form the compounds shown in the original formula equation. Check to ensure that all other ions balance.*** The NO_3^- ion appeared as nitric acid in the original equation. There are only 6 hydrogen ions to pair with the 8 nitrate ions. Therefore, 2 hydrogen ions must be added to complete this formula. If 2 hydrogen ions are added to the left side of the equation, 2 hydrogen ions must also be added to the right side of the equation.

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + SO_4^{2-} + 2H^+$$

The sulfate ion appeared as sulfuric acid in the original equation. The hydrogen ions added to the right side are used to complete the formula for sulfuric acid.

$$8HNO_3 + H_2S \longrightarrow 8NO_2 + 4H_2O + H_2SO_4$$

A final check must be made to ensure that all elements are correctly balanced.

FIGURE 19-4 As a $KMnO_4$ solution is titrated into an acidic solution of $FeSO_4$, deep purple MnO_4^- ions are reduced to colorless Mn^{2+} ions. When all Fe^{2+} ions are oxidized, MnO_4^- ions are no longer reduced to colorless Mn^{2+} ions. Thus, the first faint appearance of the MnO_4^- color indicates the end point of the titration.

SAMPLE PROBLEM 19-1

Write a balanced equation for the reaction shown in Figure 19-4. A deep purple solution of potassium permanganate is titrated into a colorless solution of iron(II) sulfate and sulfuric acid. The products are iron(III) sulfate, manganese(II) sulfate, potassium sulfate, and water—all of which are colorless.

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SOLUTION

1. *Write the formula equation if it is not given in the problem. Then write the ionic equation.*

$$KMnO_4 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$$

$$K^+ + MnO_4^- + Fe^{2+} + SO_4^{2-} + 2H^+ + SO_4^{2-} \longrightarrow 2Fe^{3+} + 3SO_4^{2-} + Mn^{2+} + SO_4^{2-} + 2K^+ + SO_4^{2-} + H_2O$$

2. *Assign oxidation numbers to each element and ion. Delete substances containing an element that does not change oxidation state.*

$$\overset{+1}{K^+} + \overset{+7\ -2}{MnO_4^-} + \overset{+2}{Fe^{2+}} + \overset{+6\ -2}{SO_4^{2-}} + \overset{+1}{2H^+} + \overset{+6\ -2}{SO_4^{2-}} \longrightarrow \overset{+3}{2Fe^{3+}} + \overset{+6\ -2}{3SO_4^{2-}} + \overset{+2}{Mn^{2+}} + \overset{+6\ -2}{SO_4^{2-}} + \overset{+1}{2K^+} + \overset{+6\ -2}{SO_4^{2-}} + \overset{+1\ -2}{H_2O}$$

Only ions or molecules whose oxidation numbers change are retained.

$$\overset{+7\ -2}{MnO_4^-} + \overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}} + \overset{+2}{Mn^{2+}}$$

3. *Write the half-reaction for oxidation.* The iron shows the increase in oxidation number. Therefore, it is oxidized.

$$\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}}$$

- *Balance the mass.* The mass is already balanced.

- *Balance the charge.*

$$\overset{+2}{Fe^{2+}} \longrightarrow \overset{+3}{Fe^{3+}} + e^-$$

4. *Write the half-reaction for reduction.* Manganese shows a change in oxidation number from +7 to +2. It is reduced.

$$\overset{+7}{MnO_4^-} \longrightarrow \overset{+2}{Mn^{2+}}$$

- *Balance the mass.* Water and hydrogen ions must be added to balance the oxygen atoms in the permanganate ion.

$$\overset{+7}{MnO_4^-} + 8H^+ \longrightarrow \overset{+2}{Mn^{2+}} + 4H_2O$$

- *Balance the charge.*

$$\overset{+7}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \overset{+2}{Mn^{2+}} + 4H_2O$$

5. *Adjust the coefficients to conserve charge.*

$$\frac{e^- \text{ lost in oxidation}}{e^- \text{ gained in reduction}} = \frac{1}{5}$$

$$5(Fe^{2+} \longrightarrow Fe^{3+} + e^-)$$

$$1(MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O)$$

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6. *Combine the half-reactions and cancel.*

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^-$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$MnO_4^- + 5Fe^{2+} + 8H^+ + \cancel{5e^-} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O + \cancel{5e^-}$$

7. *Combine ions to form compounds from the original equation.* The iron(III) product appears in the original equation as $Fe_2(SO_4)_3$. Every iron(III) sulfate molecule requires two iron ions. Therefore, the entire equation must be multiplied by 2 to provide an even number of iron ions.

$$2(5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O)$$
$$10Fe^{2+} + 2MnO_4^- + 16H^+ \longrightarrow 10Fe^{3+} + 2Mn^{2+} + 8H_2O$$

The iron(II), iron(III), manganese(II), and 2 hydrogen ions in the original equation are paired with sulfate ions. Iron(II) sulfate requires 10 sulfate ions, and sulfuric acid requires 8 sulfate ions. To balance the equation, 18 sulfate ions must be added to each side. On the product side, 15 of these ions form iron(III) sulfate, and 2 of them form manganese(II) sulfate. That leaves 1 sulfate ion unaccounted for. The permanganate ion requires the addition of 2 potassium ions to each side. These 2 potassium ions form potassium sulfate on the product side of the reaction.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Final inspection shows that atoms and charges are balanced.

PRACTICE

1. Copper reacts with hot, concentrated sulfuric acid to form copper(II) sulfate, sulfur dioxide, and water. Write and balance the equation for this reaction.

   Answer
   $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

2. Write and balance the equation for the reaction between nitric acid and potassium iodide. The products are potassium nitrate, iodine, nitrogen monoxide, and water.

   Answer
   $8HNO_3 + 6KI \longrightarrow 6KNO_3 + 3I_2 + 2NO + 4H_2O$

3. Rust occurs when iron reacts with oxygen and water to form iron(III) hydroxide. Write and balance the equation for this reaction.

   Answer
   $4Fe + 3O_2 + 6H_2O \longrightarrow 4Fe(OH)_3$

SECTION REVIEW

1. What two quantities are conserved in redox equations?
2. Why do we add H^+ and H_2O to some half-reactions and OH^- and H_2O to others?
3. Balance the following oxidation-reduction reaction:

   $Na_2SnO_2 + Bi(OH)_3 \longrightarrow Bi + Na_2SnO_3 + H_2O$

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SECTION 19-3

Objectives

- Relate chemical activity to oxidizing and reducing strength.
- Explain the concept of auto-oxidation.

Oxidizing and Reducing Agents

A **reducing agent** *is a substance that has the potential to cause another substance to be reduced.* Reducing agents lose electrons; they attain a more positive oxidation state during an oxidation-reduction reaction. Therefore, the reducing agent is the oxidized substance.

An **oxidizing agent** *is a substance that has the potential to cause another substance to be oxidized.* Oxidizing agents gain electrons and attain a more negative oxidation state during an oxidation-reduction reaction. The oxidizing agent is the reduced substance. Table 19-2 helps clarify the terms describing the oxidation-reduction process.

Strengths of Oxidizing and Reducing Agents

Different substances can be compared and rated on their relative potential as reducing and oxidizing agents. For example, the order of the elements in the activity series, found in Table 8-3 on page 266, is related to each element's tendency to lose electrons. Elements in this series lose electrons to the positively charged ions of any element below them in the series. The more active an element is, the greater its tendency to lose electrons and the better a reducing agent it is. The greater the distance is between two elements in the list, the more likely it is that a redox reaction will take place between them.

These elements and some other familiar substances are arranged in Table 19-3 according to their activity as oxidizing and reducing agents. The fluorine atom is the most highly electronegative atom. It is also the

TABLE 19-2 *Oxidation-Reduction Terminology*

Term	Change in oxidation number	Change in electron population
Oxidation	in a positive direction	loss of electrons
Reduction	in a negative direction	gain of electrons
Oxidizing agent	in a negative direction	gains electrons
Reducing agent	in a positive direction	loses electrons

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most active oxidizing agent. Because of its strong attraction for its own electrons, the fluoride ion is the weakest reducing agent. The negative ion of a strong oxidizing agent is a weak reducing agent.

The positive ion of a strong reducing agent is a weak oxidizing agent. As shown in Table 19-3, Li atoms are strong reducing agents because Li is a very active metal. When Li atoms oxidize, they produce Li^+ ions, which are unlikely to reacquire electrons, so Li^+ ions are weak oxidizing agents.

The left column of each pair also shows the relative abilities of metals listed in the table to displace other metals from their compounds. Zinc, for example, appears above copper. Thus, zinc is the more active reducing agent, and it displaces copper ions from solutions of copper compounds, as illustrated in Figure 19-5. The copper(II) ion, on the other hand, is a more active oxidizing agent than the zinc ion.

Nonmetals and some important ions also are included in the series in Table 19-3. Any reducing agent is oxidized by the oxidizing agents below it. Observe that F_2 displaces Cl^-, Br^-, and I^- ions from their solutions. Cl_2 displaces Br^- and I^- ions, and Br_2 displaces I^- ions. The equation for the displacement of Br^- by Cl_2 is as follows.

$$Cl_2 + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2$$

$$\overset{-1}{2Br^-} \longrightarrow \overset{0}{Br_2} + 2e^- \qquad \text{(oxidation)}$$

$$\overset{0}{Cl_2} + 2e^- \longrightarrow \overset{-1}{2Cl^-} \qquad \text{(reduction)}$$

In every redox reaction, there is one reducing agent and one oxidizing agent. In the preceding example, Br^- is the reducing agent and Cl_2 is the oxidizing agent.

TABLE 19-3 *Relative Strength of Oxidizing and Reducing Agents*

Reducing agents	Oxidizing agents
Li	Li^+
K	K^+
Ca	Ca^{2+}
Na	Na^+
Mg	Mg^{2+}
Al	Al^{3+}
Zn	Zn^{2+}
Cr	Cr^{3+}
Fe	Fe^{2+}
Ni	Ni^{2+}
Sn	Sn^{2+}
Pb	Pb^{2+}
H_2	H_3O^+
H_2S	S
Cu	Cu^{2+}
I^-	I_2
MnO_4^{2-}	MnO_4^-
Fe^{2+}	Fe^{3+}
Hg	Hg_2^{2+}
Ag	Ag^+
NO_2^-	NO_3^-
Br^-	Br_2
Mn^{2+}	MnO_2
SO_2	H_2SO_4 (conc.)
Cr^{3+}	$Cr_2O_7^{2-}$
Cl^-	Cl_2
Mn^{2+}	MnO_4^-
F^-	F_2

Increasing strength ↑ (Reducing agents) — Increasing strength ↓ (Oxidizing agents)

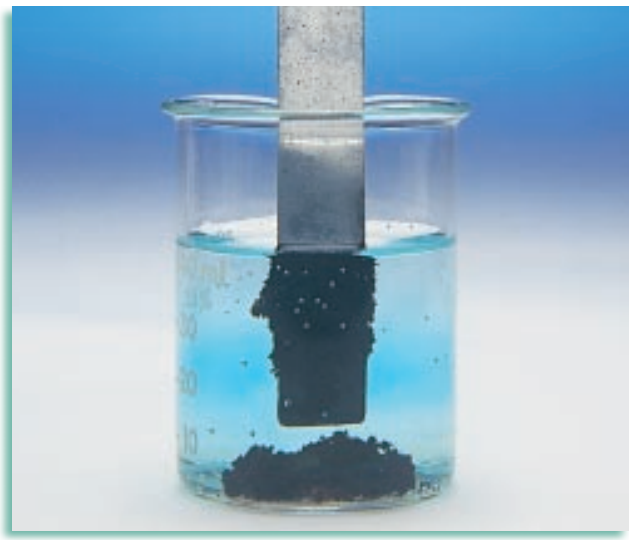

FIGURE 19-5 Zinc displaces copper ions from a copper(II) sulfate solution. Metallic copper precipitates.

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Quick LAB

Redox Reactions

Wear Safety Goggles and an Apron.

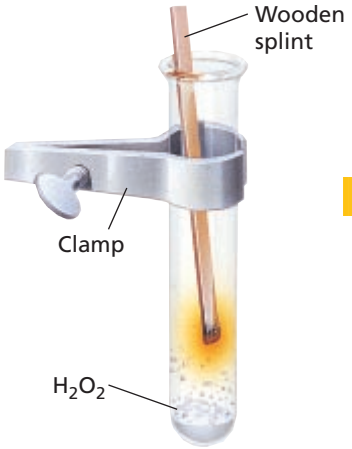
Materials

- aluminum foil
- beaker, 250 mL
- 1 M copper(II) chloride solution, $CuCl_2$
- 3% hydrogen peroxide
- manganese dioxide
- metric ruler
- scissors
- test-tube clamp
- test tube, 16 × 150 mm
- wooden splint

Procedure

Record all your results in a data table.

1. Put 10 mL of hydrogen peroxide in a test tube, and add a small amount of manganese dioxide (equal to the size of about half a pea). What is the result?



2. Insert a glowing wooden splint into the test tube (see diagram). What is the result? If oxygen is produced, a glowing wooden splint inserted into the test tube will glow brighter.
3. Fill the 250 mL beaker halfway with the copper(II) chloride solution.
4. Cut foil into 2 cm × 12 cm strips.
5. Add the aluminum strips to the copper(II) chloride solution. Use a glass rod to stir the mixture, and observe for 12 to 15 minutes. What is the result?

Discussion

1. Write balanced equations showing what happened in each of the reactions.
2. Write a conclusion for the two experiments.

Autooxidation

Some substances can be both reduced and oxidized easily. For example, peroxide ions, O_2^{2-}, have a relatively unstable covalent bond between the two oxygen atoms. The electron-dot formula is written as follows.

$$\left[:\ddot{O}:\ddot{O}:\right]^{2-}$$

Each oxygen atom has an oxidation number of –1. The peroxide ion structure represents an intermediate oxidation state between O_2 and O^{2-}. Therefore, the peroxide ion is highly reactive.

Hydrogen peroxide, H_2O_2, contains the reactive peroxide ion. It decomposes into water and molecular oxygen, as shown in the equation below.

$$2\overset{-1}{H_2O_2} \longrightarrow 2\overset{-2}{H_2O} + \overset{0}{O_2}$$

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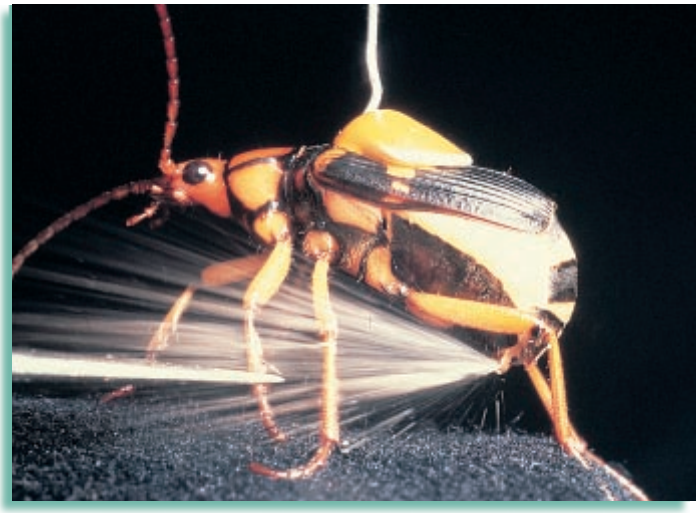

FIGURE 19-6 A bombardier beetle can repel large predators such as frogs with a chemical defense mechanism that uses the auto-oxidation of hydrogen peroxide.

Notice that in this reaction, hydrogen peroxide is both oxidized and reduced. Oxygen atoms that become part of gaseous oxygen molecules are oxidized. The oxidation number of theses oxygen atoms increases from –1 to 0. Oxygen atoms that become part of water are reduced. The oxidation number of these oxygen atoms decreases from –1 to –2. *A process in which a substance acts as both an oxidizing agent and a reducing agent is called* **autooxidation.** A substance that undergoes autooxidation is both *self-oxidizing* and *self-reducing.*

The bombardier beetle defends itself by spraying its enemies with an unpleasant hot chemical mixture as shown in Figure 19-6. The catalyzed autooxidation of hydrogen peroxide produces hot oxygen gas. This gas gives the insect an ability to eject irritating chemicals from its abdomen with explosive force.

SECTION REVIEW

1. Describe the chemical activity of the alkali metals and of the halogens on the basis of oxidizing and reducing strength.

2. The photo on the left depicts two redox reactions. Use them to answer the following questions:
   a. When zinc is wrapped around an iron nail, is the iron reduced or oxidized?
   b. When copper is wrapped around an iron nail, is the iron reduced or oxidized?
3. Would Cl_2 be reduced by I^-? Explain.
4. Which is the stronger oxidizing agent in each of the following pairs?
   Cu^{2+} or Al^{3+}, H_2 or H_3O^+, Cr or Cu?
5. What is meant by *autooxidation*?

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SECTION 19-4

Electrochemistry

Objectives

- Explain what is required for an electrochemical cell.
- Describe the nature of voltaic cells.
- Describe the nature of electrolytic cells.
- Explain the process of electroplating.
- Describe the chemistry of a rechargeable cell.
- Calculate cell potentials from a table of standard electrode potentials.

Oxidation-reduction reactions involve energy changes. Because these reactions involve electron transfer, the net *release* or net *absorption* of energy can occur in the form of electrical energy rather than as heat. This property allows for a great many practical applications of redox reactions. It also makes possible quantitative predictions and comparisons of the oxidizing and reducing abilities of different substances. *The branch of chemistry that deals with electricity-related applications of oxidation-reduction reactions is called* **electrochemistry.**

Electrochemical Cells

Oxidation-reduction reactions involve a transfer of electrons from the substance oxidized to the substance reduced. If the two substances are in contact with one another, a transfer of energy as heat accompanies the electron transfer. In Figure 19-7 a zinc strip is in contact with a copper(II) sulfate solution. The zinc strip loses electrons to the copper(II) ions in solution. Copper(II) ions accept the electrons and fall out of solution as copper atoms. As electrons are transferred between zinc atoms and copper(II) ions, energy is released as heat, as indicated by the rise in temperature.

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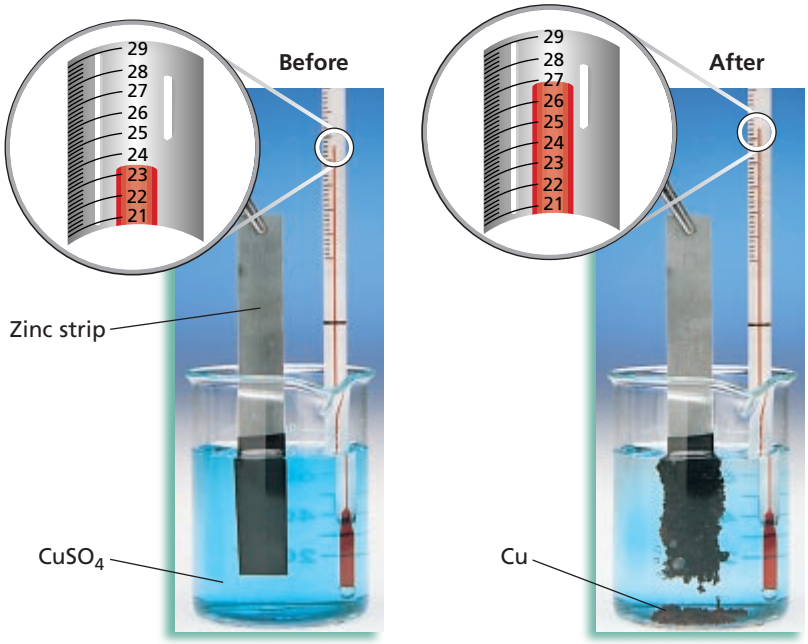

FIGURE 19-7 Heat energy given off when electrons are transferred directly from Zn atoms to Cu^{2+} ions causes the temperature of the aqueous $CuSO_4$ solution to rise.

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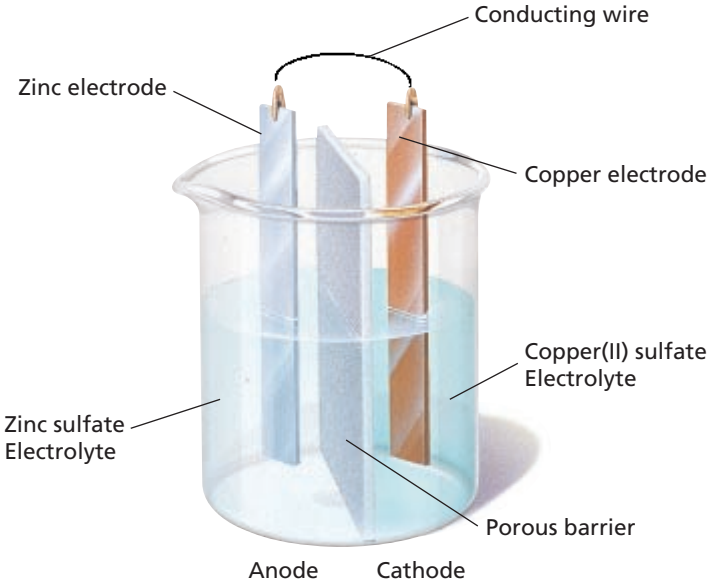

FIGURE 19-8 An electrochemical cell consists of two electrodes. Each electrode is in contact with an electrolyte; the electrode and the electrolyte make up a half-cell. The two electrodes are connected by a wire, and a porous barrier separates the two electrolytes.

If, however, we separate the substance that is oxidized during the reaction from the substance that is reduced during the reaction, the electron transfer is accompanied by a transfer of electrical energy instead of heat. One means of separating oxidation and reduction half-reactions is with a *porous barrier.* This barrier prevents the metal atoms of one half-reaction from mixing with the ions of the other half-reaction. Ions in the two solutions can move through the porous barrier. Electrons can be transferred from one side to the other through an external connecting wire. Electric current moves in a closed loop path, or *circuit,* so this movement of electrons through the wire is balanced by the movement of ions in solution.

Altering the system in Figure 19-7 so that electrical current is produced instead of heat would simply involve separating the copper and zinc, as shown in Figure 19-8. The Zn strip is in an aqueous solution of $ZnSO_4$. The Cu strip is in an aqueous solution of $CuSO_4$. Both solutions conduct electricity, so, as you learned in Chapter 14, they are classified as electrolytes. *An* **electrode** *is a conductor used to establish electrical contact with a nonmetallic part of a circuit, such as an electrolyte*. In Figure 19-8, the Zn and Cu strips are electrodes. *A single electrode immersed in a solution of its ions is a* **half-cell.** The Zn strip in aqueous $ZnSO_4$ is an **anode,** *the electrode where oxidation takes place*. The Cu strip in $CuSO_4$ is a **cathode,** *the electrode where reduction takes place*. The copper half-cell can be written as Cu^{2+}/Cu, and the zinc half-cell can be written as Zn^{2+}/Zn. The two half-cells together make an electrochemical cell. *An* **electrochemical cell** is a *system of electrodes and electrolytes in which either chemical reactions produce electrical energy or an electric current produces chemical change*. An electrochemical cell may be represented by the following notation: anode | cathode. For the example, the cell made up of zinc and copper could be written as Zn | Cu. There are two types of electrochemical cells: voltaic (also called galvanic) and electrolytic.

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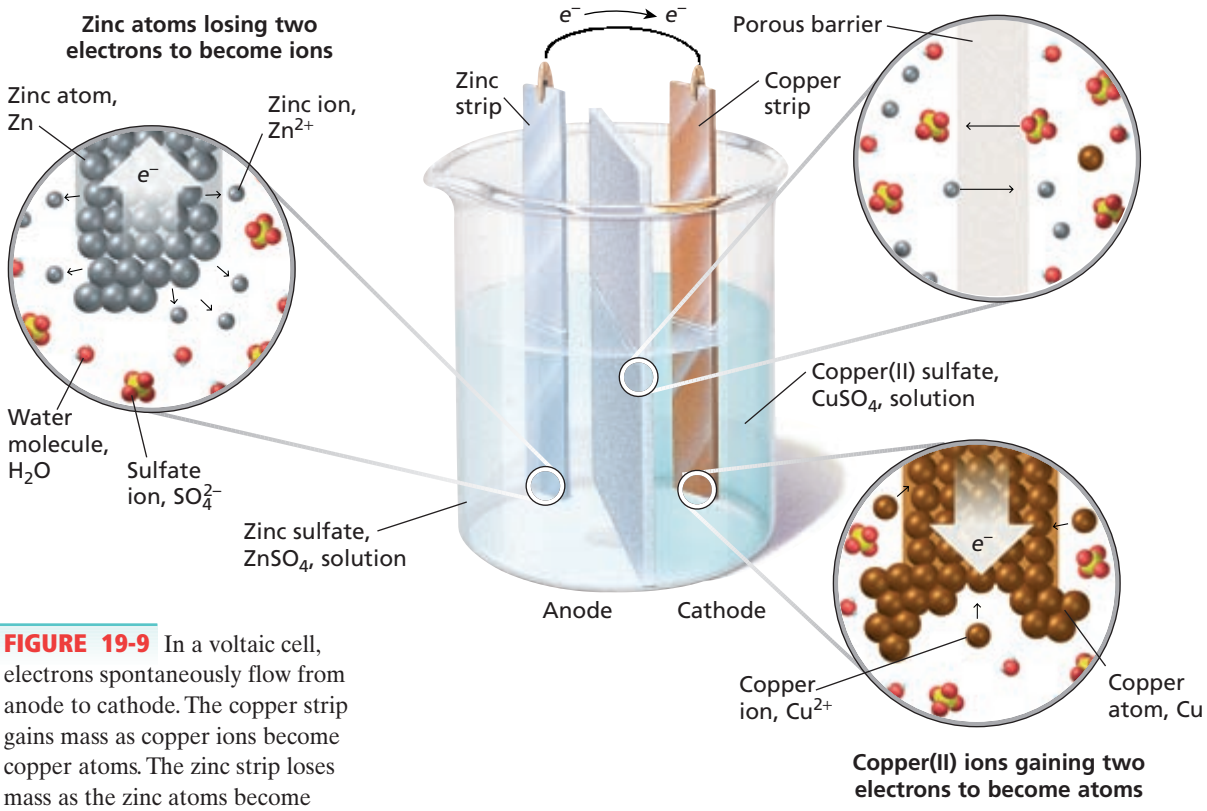

FIGURE 19-9 In a voltaic cell, electrons spontaneously flow from anode to cathode. The copper strip gains mass as copper ions become copper atoms. The zinc strip loses mass as the zinc atoms become zinc ions.

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Module 10: Electrochemical Cells

Voltaic Cells

If the redox reaction in an electrochemical cell occurs spontaneously and produces electrical energy, the cell is a **voltaic cell.** Cations in the solution are reduced when they gain electrons at the surface of the cathode to become metal atoms. This half-reaction for the voltaic cell shown in Figure 19-9 is as follows.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

The half-reaction occurring at the anode is as follows.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

Electrons given up at the anode pass along the external connecting wire to the cathode.

The movement of electrons through the wire must be balanced by a movement of ions in the solution. Anions move toward the anode to replace the negatively charged electrons that are moving away. Cations move toward the cathode as positive charge is lost through reduction. Thus, in Figure 19-9, sulfate ions in the $CuSO_4$ solution can move through the barrier into the $ZnSO_4$ solution. Likewise, the Zn^{2+} ions pass through the barrier into the $CuSO_4$ solution.

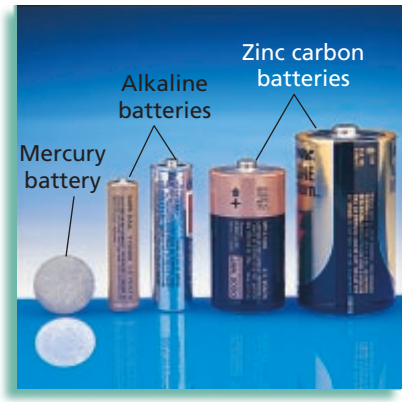

FIGURE 19-10 Many common batteries are simple voltaic dry cells.

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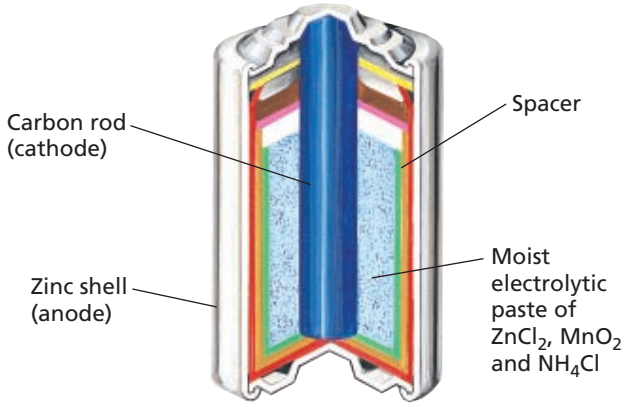

FIGURE 19-11 In a zinc dry cell, zinc is oxidized to Zn^{2+} at the anode, and manganese(IV) is reduced to manganese(III) at the cathode.

The dry cells pictured in Figure 19-10 are common sources of electrical energy. Like the wet cell previously described, dry cells are voltaic cells. The three most common types of dry cells are the zinc-carbon battery, the alkaline battery, and the mercury battery. They differ in the substances being oxidized and reduced.

Zinc-Carbon Dry Cells

Batteries such as those used in flashlights are zinc-carbon dry cells. These cells consist of a zinc container, which serves as the anode, filled with a moist paste of MnO_2, graphite, and NH_4Cl, as illustrated in Figure 19-11. When the external circuit is closed, zinc atoms are oxidized at the negative electrode, or anode.

$$\overset{0}{Zn}(s) \longrightarrow \overset{+2}{Zn^{2+}}(aq) + 2e^-$$

Electrons move across the circuit and reenter the cell through the carbon rod. The carbon rod is the cathode or positive electrode. Here MnO_2 is reduced in the presence of H_2O according to the following half-reaction.

$$2\overset{+4}{MnO_2}(s) + H_2O(l) + 2e^- \longrightarrow \overset{+3}{Mn_2O_3}(s) + 2OH^-(aq)$$

Alkaline Batteries

The batteries found in a small, portable cassette player or other small electronic device are frequently alkaline dry cells. These cells do not have a carbon rod cathode, as in the zinc-carbon cell. The absence of the carbon rod allows them to be smaller. Figure 19-12 shows a model of an alkaline battery. This cell uses a paste of Zn metal and potassium hydroxide instead of a solid metal anode. The half-reaction at the anode is as follows.

$$\overset{0}{Zn}(s) + 2OH^-(aq) \longrightarrow \overset{+2}{Zn}(OH)_2(s) + 2e^-$$

The reduction half-reaction, the reaction at the cathode, is exactly the same as that for the zinc-carbon dry cell.

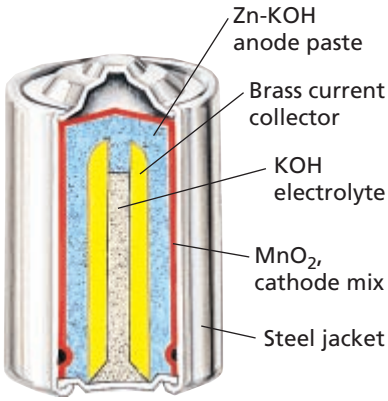

FIGURE 19-12 KOH makes the electrolyte paste in this battery basic. Thus, it is called an alkaline dry cell.

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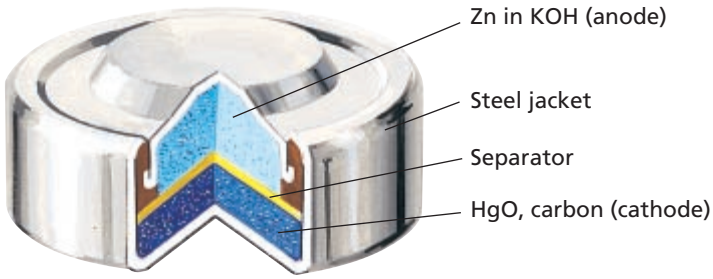

FIGURE 19-13 It is important that mercury batteries be recycled and not just discarded because mercury is a poisonous substance.

Mercury Batteries

The tiny batteries found in hearing aids, calculators, and camera flashes are mercury batteries, as shown in Figure 19-13. The anode half-reaction is identical to that found in the alkaline dry cell. However, the cathode, or reduction, half-reaction is different. The cathode half-reaction is described by the following equation.

$$\overset{+2}{\mathrm{Hg}}\mathrm{O}(s) + \mathrm{H_2O}(l) + 2e^- \longrightarrow \overset{0}{\mathrm{Hg}}(l) + 2\mathrm{OH}^-(aq)$$

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Module 10: Electrochemical Cells

Electrolytic Cells

Some oxidation-reduction reactions do not occur spontaneously, but can be driven by electrical energy. *The process in which an electric current is used to produce an oxidation-reduction reaction is* **electrolysis.** *If electrical energy is required to produce a redox reaction and bring about a chemical change in an electrochemical cell, it is an* **electrolytic cell.** Most commercial uses of redox reactions make use of electrolytic cells.

An electrolytic cell is depicted in Figure 19-14. The electrode of the cell connected to the negative terminal of the battery acquires an excess of electrons and becomes the cathode of the electrolytic cell. The electrode of the cell connected to the positive terminal of the battery loses electrons to the battery; it is the anode of the electrolytic cell. The battery can be thought of as an electron pump simultaneously supplying electrons to the cathode and recovering electrons from the anode. This energy input from the battery drives the electrode reactions in the electrolytic cell.

A comparison of electrolytic and voltaic cells can be seen in Figure 19-14. The voltaic cell shown in Figure 19-14 has a copper cathode and a zinc anode. If a battery is connected so that the positive terminal contacts the copper electrode and the negative terminal contacts the zinc electrode, the electrons flow in the opposite direction. The battery forces the cell to reverse its reaction; the zinc electrode becomes the cathode, and the copper electrode becomes the anode. The half-reaction at the anode, in which copper metal is oxidized, can be written as follows.

$$\overset{0}{\mathrm{Cu}} \longrightarrow \overset{+2}{\mathrm{Cu}}^{2+} + 2e^-$$

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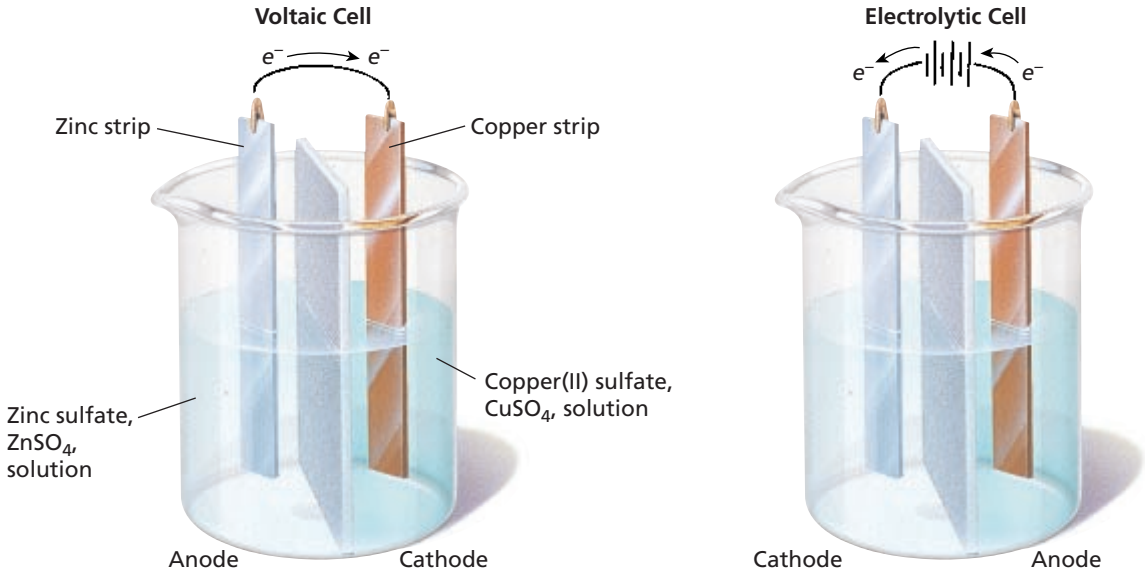

FIGURE 19-14 The direction in which the electrons move reverses if a voltaic cell is connected to a direct current source to become an electrolytic cell.

The reduction half-reaction of zinc at the cathode is written as follows.

$$\overset{+2}{Zn^{2+}} + 2e^- \longrightarrow \overset{0}{Zn}$$

There are two important differences between the voltaic cell and the electrolytic cell.

1. The anode and cathode of an electrolytic cell are connected to a battery or other direct-current source, whereas a voltaic cell serves as a source of electrical energy.
2. Electrolytic cells are those in which electrical energy from an external source causes *nonspontaneous* redox reactions to occur. Voltaic cells are those in which *spontaneous* redox reactions produce electricity. In an electrolytic cell, electrical energy is converted to chemical energy; in a voltaic cell, chemical energy is converted to electrical energy.

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Electroplating

Metals such as copper, silver, and gold are difficult to oxidize. In an electrolytic cell, these inactive metals form ions at an anode that are easily reduced at a cathode. This type of cell allows solid metal from one electrode to be deposited on the other electrode. *An electrolytic process in which a metal ion is reduced and a solid metal is deposited on a surface is called* **electroplating.**

An electroplating cell contains a solution of a salt of the plating metal. It has an object to be plated (the cathode) and a piece of the plating metal (the anode). A silver-plating cell contains a solution of a soluble silver salt and a silver anode. The cathode is the object to be plated. The silver anode is connected to the positive electrode of a battery or to some other source of direct current. The object to be plated is connected to the negative electrode.

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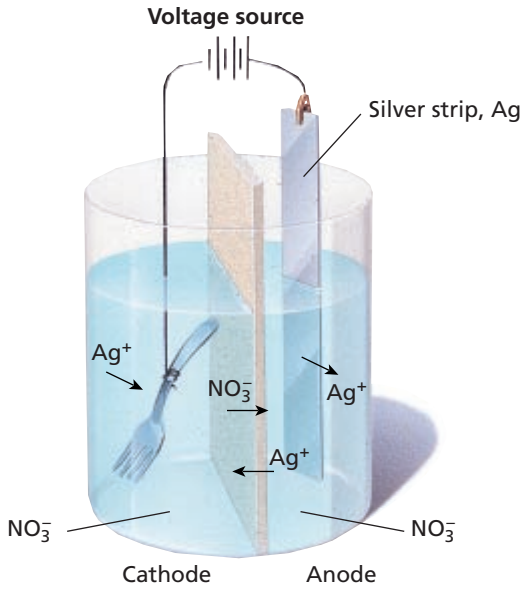

FIGURE 19-15 Electroplating is often used to avoid corrosion (a redox reaction) at the object's surface by putting a layer of an inactive metal on a more-active metal.

A cell in which silver is being electroplated onto a fork can be seen in Figure 19-15. Silver ions are reduced at the cathode according to the following equation and deposited as metallic silver when electrons flow through the circuit.

$$\overset{+1}{Ag^+} + e^- \longrightarrow \overset{0}{Ag}$$

Meanwhile, metallic silver is removed from the anode as ions. Silver atoms are oxidized at the anode according to the following half-reaction.

$$\overset{0}{Ag} \longrightarrow \overset{+1}{Ag^+} + e^-$$

This action maintains the Ag^+ ion concentration of the solution. Thus, in effect, silver is transferred from the anode to the cathode of the cell.

Rechargeable Cells

A rechargeable cell combines the oxidation-reduction chemistry of both voltaic cells and electrolytic cells. When a rechargeable cell converts chemical energy to electrical energy, it operates as a voltaic cell. But when the cell is recharged, it operates as an electrolytic cell, converting electrical energy to chemical energy.

The standard 12 V automobile battery, shown in Figure 19-16, is a set of six rechargeable cells. The anode in each cell is lead submerged in a solution of H_2SO_4. The anode half-reaction is described by the following equation.

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

Electrons move through the circuit to the cathode, where PbO_2 is reduced according to the following equation.

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

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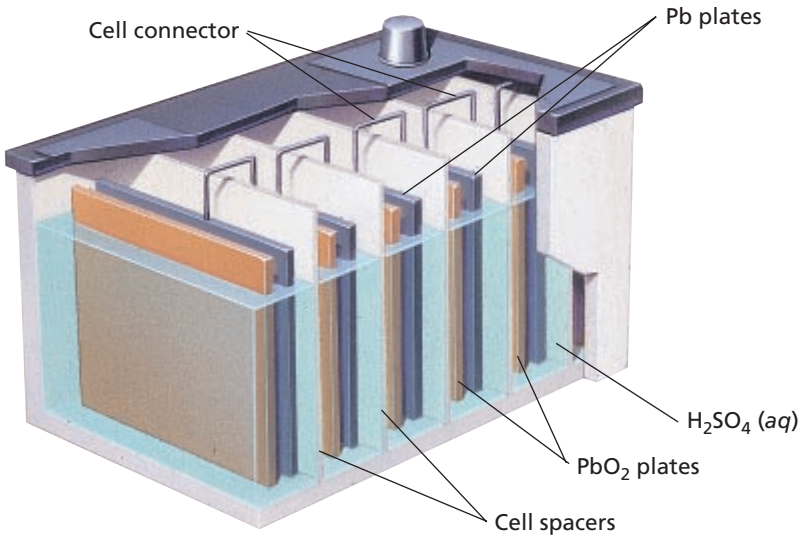

FIGURE 19-16 The rechargeable cells of a car battery produce electricity from reactions between lead(IV) oxide, lead, and sulfuric acid.

The net oxidation-reduction reaction for the discharge cycle is described by the following chemical equation.

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

A car's battery produces the electric energy needed to start its engine. Sulfuric acid, present as its ions, is consumed, and lead(II) sulfate accumulates as a white powder on the electrodes. Once the car is running, the half-reactions are reversed by a voltage produced by the alternator. The Pb, PbO_2, and H_2SO_4 are regenerated. A battery can be recharged as long as all reactants necessary for the electrolytic reaction are present, and all reactions are reversible.

Electrode Potentials

Reconsider the voltaic cell shown in Figure 19-9. There are two electrodes, Zn and Cu. According to Table 19-3, these two metals each have different tendencies for accepting electrons. *This tendency for the half-reaction of either copper or zinc to occur as a reduction half-reaction in an electrochemical cell can be quantified as a* **reduction potential.** There are two half-cells in Figure 19-9: a strip of zinc placed in a solution of $ZnSO_4$ and a strip of copper placed in a solution of $CuSO_4$. *The difference in potential between an electrode and its solution is known as its* **electrode potential.** When these two half-cells are connected and the reaction begins, a difference in potential is observed between the electrodes. This potential difference, or voltage, is a measure of the energy required to move a certain electric charge between the electrodes. Potential difference is measured in volts. A voltmeter connected across the Cu | Zn voltaic cell measures a potential difference of about 1.10 V when the solution concentrations of Zn^{2+} and Cu^{2+} ions are each 1 M.

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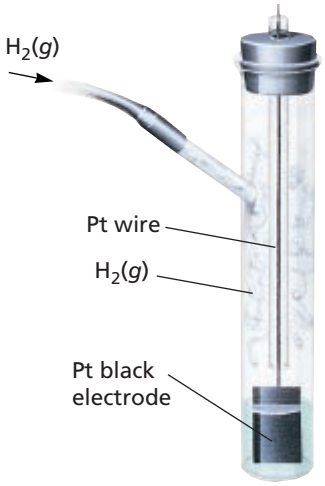

FIGURE 19-17 A hydrogen electrode is the standard reference electrode for measuring electrode potentials. The electrode surface in contact with the solution is actually a layer of hydrogen adsorbed onto the surface of the platinum.

The potential difference measured across the complete voltaic cell roughly equals the sum of the electrode potentials for the two half-reactions. But while the potential difference across a voltaic cell is easily measured, there is no way to measure an individual electrode potential directly. This is because there can be no transfer of electrons unless both the anode and the cathode are connected to form a complete circuit. A relative value for the potential of a half-reaction can be determined by connecting it to a standard half-cell as a reference. This standard half-cell, shown in Figure 19-17, is called a standard hydrogen electrode, or SHE. It consists of a platinum electrode dipped into a 1.00 M acid solution surrounded by hydrogen gas at 1 atm pressure and 25°C. Other electrodes are ranked according to their ability to reduce hydrogen under these conditions.

The anodic reaction for the standard hydrogen electrode is described by the forward half-reaction in the following equilibrium equation.

$$\overset{0}{H_2(g)} \rightleftharpoons \overset{+1}{2H^+(aq)} + 2e^-$$

The cathodic half-reaction is the reverse. An arbitrary potential of 0.00 V is assigned to both of these half-reactions. Therefore, any voltage measurement obtained is attributed to the half-cell connected to the SHE. *A half-cell potential measured relative to a potential of zero for the standard hydrogen electrode is a* **standard electrode potential,** E^0. Electrode potentials are expressed as potentials for reduction. These reduction potentials provide a reliable indication of the tendency of a substance to be reduced. Half-reactions for some common electrodes and their standard electrode potentials are listed in Table 19-4.

Positive E^0 values indicate that hydrogen is more willing to give up its electrons than the other electrode. Half-reactions with positive reduction potentials are favored. Effective oxidizing agents, such as Cu and F_2, have positive E^0 values. Half-reactions with negative reduction potentials are not favored; these half-reactions prefer oxidation over reduction. Negative E^0 values indicate that the metal or other electrode is more willing to give up electrons than hydrogen. Effective reducing agents, such as Li and Zn, have negative E^0 values. When a half-reaction

FIGURE 19-18 The electrode potentials of zinc and copper half-cells are measured by coupling them with a standard hydrogen electrode.

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TABLE 19-4 Standard Reduction Potentials

Half-cell reaction	Standard electrode potential, E^0 (in volts)	Half-cell reaction	Standard electrode potential, E^0 (in volts)
$F_2 + 2e^- \rightleftarrows 2F^-$	+2.87	$Fe^{3+} + 3e^- \rightleftarrows Fe$	−0.04
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$	+1.50	$Pb^{2+} + 2e^- \rightleftarrows Pb$	−0.13
$Au^{3+} + 3e^- \rightleftarrows Au$	+1.50	$Sn^{2+} + 2e^- \rightleftarrows Sn$	−0.14
$Cl_2 + 2e^- \rightleftarrows 2Cl^-$	+1.36	$Ni^{2+} + 2e^- \rightleftarrows Ni$	−0.26
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O$	+1.23	$Co^{2+} + 2e^- \rightleftarrows Co$	−0.28
$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	+1.22	$Cd^{2+} + 2e^- \rightleftarrows Cd$	−0.40
$Br_2 + 2e^- \rightleftarrows 2Br^-$	+1.07	$Fe^{2+} + 2e^- \rightleftarrows Fe$	−0.45
$Hg^{2+} + 2e^- \rightleftarrows Hg$	+0.85	$S + 2e^- \rightleftarrows S^{2-}$	−0.48
$Ag^+ + e^- \rightleftarrows Ag$	+0.80	$Cr^{3+} + 3e^- \rightleftarrows Cr$	−0.74
$Hg_2^{2+} + 2e^- \rightleftarrows 2Hg$	+0.80	$Zn^{2+} + 2e^- \rightleftarrows Zn$	−0.76
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.77	$Al^{3+} + 3e^- \rightleftarrows Al$	−1.66
$MnO_4^- + e^- \rightleftarrows MnO_4^{2-}$	+0.56	$Mg^{2+} + 2e^- \rightleftarrows Mg$	−2.37
$I_2 + 2e^- \rightleftarrows 2I^-$	+0.54	$Na^+ + e^- \rightleftarrows Na$	−2.71
$Cu^{2+} + 2e^- \rightleftarrows Cu$	+0.34	$Ca^{2+} + 2e^- \rightleftarrows Ca$	−2.87
$Cu^{2+} + e^- \rightleftarrows Cu^+$	+0.15	$Ba^{2+} + 2e^- \rightleftarrows Ba$	−2.91
$S + 2H^+(aq) + 2e^- \rightleftarrows H_2S(aq)$	+0.14	$K^+ + e^- \rightleftarrows K$	−2.93
$2H^+(aq) + 2e^- \rightleftarrows H_2$	0.00	$Li^+ + e^- \rightleftarrows Li$	−3.04

is written as an oxidation reaction, the sign of its electrode potential is changed as shown for the oxidation and reduction half-reactions for zinc.

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^0 = -0.76\ V$$
$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad E^0 = +0.76\ V$$

To measure the reduction potential of a zinc half-cell, it is connected to a standard hydrogen electrode, as in Figure 19-18. The potential difference across the cell is –0.76 V. The negative number indicates that electrons flow through the external circuit from the zinc electrode, where zinc is oxidized, to the hydrogen electrode, where aqueous hydrogen ions are reduced.

A copper half-cell coupled with the standard hydrogen electrode gives a potential difference measurement of +0.34 V. This positive number indicates that $Cu^{2+}(aq)$ ions are more readily reduced than $H^+(aq)$ ions.

Standard electrode potentials can be used to predict if a redox reaction will occur naturally. A naturally occurring reaction will have a positive value for E^0_{cell}, which is calculated using the following equation.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

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Module 10: Electrochemical Cells

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When evaluating the two half-reactions in a voltaic cell, the half-reaction with the more negative standard reduction potential is the anode. Oxidation occurs at the anode, so the half-cell reaction is the reverse of the reduction reaction found in Table 19-4. When a reaction is reversed, the actual half-cell potential is the negative of the standard reduction potential. For this reason, the total potential of a cell is calculated by subtracting the standard reduction potential for the reaction at the anode (E^0_{anode}) from the standard reduction potential for the reaction at the cathode ($E^0_{cathode}$).

Consider cells made from Fe in a solution of $Fe(NO_3)_3$ and Ag in a solution of $AgNO_3$. Table 19-4 gives the following half-reactions and E^0 values for these half-cells.

$$Fe^{3+}(aq) + 3e^- \longrightarrow Fe(s) \qquad E^0 = -0.04\ V$$
$$3Ag^+(aq) + 3e^- \longrightarrow 3Ag(s) \qquad E^0 = +0.80\ V$$

Fe in $Fe(NO_3)_3$ is the anode because it has the lower reduction potential, and Ag in $AgNO_3$ is therefore the cathode. The overall cell reaction is

$$3Ag^+(aq) + Fe(s) \longrightarrow 3Ag^+(s) + Fe^{3+}(aq)$$

The reduction of silver ions is multiplied by 3 so that the number of electrons lost in that half-reaction equals the number of electrons gained in the oxidation of iron. The standard reduction potentials for the anode and cathode are as follows.

$$E^0_{anode} = -0.04\ V$$
$$E^0_{cathode} = +0.80\ V$$

Note that when a half-reaction is multiplied by a constant, the E^0 value is not multiplied but remains the same.

So the potential for this cell can be calculated as follows.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$E^0_{cell} = +0.80\ V - (-0.04\ V) = 0.84\ V$$

If the calculated value for E^0_{cell} were negative, the reaction would not occur naturally in the direction written, so it would not occur in a voltaic cell. It could be made to occur in an electrolytic cell.

SECTION REVIEW

1. What is a voltaic cell?
2. Describe an electrolytic cell.
3. Explain the process of electroplating.
4. What is a rechargeable cell?
5. What is electrode potential, and how is it used to calculate information about an electrochemical reaction?
6. Given the Na^+/Na and K^+/K half-cells, determine the overall electrochemical reaction that proceeds spontaneously and the E^0 value.

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CHAPTER 19 REVIEW

CHAPTER SUMMARY

19-1

- Oxidation numbers are assigned by the set of rules listed in Table 19-1.
- Oxidation-reduction reactions consist of two half-reactions that must occur simultaneously.
- Oxidation-reduction reactions are identified by examining the reactants and products for changes in oxidation numbers of their constituent atoms.
- Oxidation involves the loss of electrons, and reduction involves the gain of electrons.

Vocabulary

half-reaction (593)
oxidation (592)
oxidation-reduction reaction (593)
oxidized (592)
redox reaction (593)
reduced (593)
reduction (593)

19-2

- Both charge and mass are conserved in a balanced redox equation.
- In the half-reaction method for balancing equations, oxidation and reduction equations are balanced separately for atoms and charge. Then they are combined to give a complete balanced equation.

19-3

- In redox reactions, the substance that is *reduced* acts as an *oxidizing agent* because it *acquires* electrons from the substance oxidized.
- The substance that is *oxidized* in a redox reaction is the *reducing agent* because it *supplies* the electrons to the substance reduced.

Vocabulary

autooxidation (605)
oxidizing agent (602)
reducing agent (602)

19-4

- Some oxidation-reduction reactions that occur naturally can be sources of electrical energy in voltaic cells. Other oxidation-reduction reactions that do not occur naturally can be driven by an external source of electrical energy in electrolytic cells; this process is called electrolysis.
- An electrode and its electrolyte in an electrochemical cell are called a half-cell.
- The potential difference between the electrode and its solution is called the electrode potential. The sum of the electrode potentials of the two half-reactions of an electrochemical cell is roughly equal to the potential difference across the cell.
- Standard electrode potentials are measured relative to a standard hydrogen electrode. They indicate the relative strengths of substances as oxidizing and reducing agents.

Vocabulary

anode (607)
cathode (607)
electrochemical cell (607)
electrochemistry (606)
electrode (607)
electrode potential (613)
electrolysis (610)
electrolytic cell (610)
electroplating (611)
half-cell (607)
reduction potential (613)
standard electrode potential (614)
voltaic cell (608)

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REVIEWING CONCEPTS

1. a. Distinguish between the processes of oxidation and reduction.
b. Write an equation to illustrate each. (19-1)

2. Which of the following are redox reactions?
a. $2Na + Cl_2 \longrightarrow 2NaCl$
b. $C + O_2 \longrightarrow CO_2$
c. $2H_2O \longrightarrow 2H_2 + O_2$
d. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
e. $NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$
f. $2KClO_3 \longrightarrow 2KCl + 3O_2$
g. $H_2 + Cl_2 \longrightarrow 2HCl$
h. $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$
i. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$ (19-1)

3. For each oxidation-reduction reaction in the previous question, identify what is oxidized and what is reduced. (19-1)

4. a. Identify the most active reducing agent among all common elements.
b. Why are all of the elements in its group in the periodic table very active reducing agents?
c. Identify the most active oxidizing agent among the common elements. (19-3)

5. Based on Table 19-3, identify the strongest and weakest reducing agents among the substances listed within each of the following groupings:
a. Ca, Ag, Sn, Cl^-
b. Fe, Hg, Al, Br^-
c. F^-, Pb, Mn^{2+}, Na
d. Cr^{3+}, Cu^{2+}, NO_3^-, K^+
e. Cl_2, S, Zn^{2+}, Ag^+
f. Li^+, F_2, Ni^{2+}, Fe^{3+} (19-3)

6. Use Table 19-3 to respond to each of the following:
a. Would Al be oxidized by Ni^{2+}?
b. Would Cu be oxidized by Ag^+?
c. Would Pb be oxidized by Na^+?
d. Would F_2 be reduced by Cl^-?
e. Would Br_2 be reduced by Cl^-? (19-3)

7. Distinguish between a voltaic cell and an electrolytic cell in terms of the nature of the reaction involved. (19-4)

8. a. What is electroplating?
b. Distinguish between the nature of the anode and cathode in such a process. (19-4)

9. a. Explain what is meant by the potential difference between the two electrodes in an electrochemical cell.
b. How, and in what units, is this potential difference measured? (19-4)

10. The standard hydrogen electrode is assigned an electrode potential of 0.00 V. Explain why this voltage is assigned. (19-4)

11. a. What information is provided by the electrode potential of a given half-cell?
b. What does the relative value of the potential of a given half-reaction indicate about its oxidation-reduction tendency? (19-4)

PROBLEMS

Redox Equations

12. Each of the following atom/ion pairs undergoes the oxidation number change indicated below. For each pair, determine whether oxidation or reduction has occurred, and then write the electronic equation indicating the corresponding number of electrons lost or gained.
a. $K \longrightarrow K^+$
b. $S \longrightarrow S^{2-}$
c. $Mg \longrightarrow Mg^{2+}$
d. $F^- \longrightarrow F_2$
e. $H_2 \longrightarrow H^+$
f. $O_2 \longrightarrow O^{2-}$
g. $Fe^{3+} \longrightarrow Fe^{2+}$
h. $Mn^{2+} \longrightarrow MnO_4^-$

13. Identify the following reactions as redox or nonredox:
a. $2NH_4Cl(aq) + Ca(OH)_2(aq) \longrightarrow 2NH_3(aq) + 2H_2O(l) + CaCl_2(aq)$
b. $2HNO_3(aq) + 3H_2S(g) \longrightarrow 2NO(g) + 4H_2O(l) + 3S(s)$
c. $[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + [Be(H_2O)_3OH]^+(aq)$

14. Arrange the following in order of increasing oxidation number of the xenon atom:
$CsXeF_8$, Xe, XeF_2, $XeOF_2$, XeO_3, XeF

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15. Determine the oxidation number of each atom indicated in the following:

a. H_2
b. H_2O
c. Al
d. MgO
e. Al_2S_3
f. HNO_3
g. H_2SO_4
h. $Ca(OH)_2$
i. $Fe(NO_3)_2$
j. O_2

16. Balance the oxidation-reduction equation below by using the half-reaction method in response to each requested step. (Hint: See Sample Problem 19-1.)

$$K + H_2O \longrightarrow KOH + H_2$$

a. Write the ionic equation, and assign oxidation numbers to all atoms to determine what is oxidized and what is reduced.
b. Write the equation for the reduction, and balance it for both atoms and charge.
c. Write the equation for the oxidation, and balance it for both atoms and charge.
d. Adjust the oxidation and reduction equations by multiplying the coefficients as needed so that electrons lost equal electrons gained, and add the two resulting equations.
e. Add species as necessary to balance the overall formula equation.

17. Use the method in the previous problem to balance each of the reactions below.

a. $HI + HNO_2 \longrightarrow NO + I_2 + H_2O$
b. $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

18. Balance the equation for the reaction in which hot, concentrated sulfuric acid reacts with zinc to form zinc sulfate, hydrogen sulfide, and water.

Voltaic and Electrolytic Cells

19. For each of the following pairs of half-cells, determine the overall electrochemical reaction that proceeds spontaneously:

a. Cu^{2+}/Cu, Ag^{+}/Ag
b. Cd^{2+}/Cd, Co^{2+}/Co
c. Na^{+}/Na, Ni^{2+}/Ni
d. I_2/I^-, Br_2/Br^-

20. Determine the values of E^0 for the cells in the previous problem.

21. Suppose chemists had chosen to make the $I_2 + 2e^- \rightleftharpoons 2I^-$ half-cell the standard electrode and had assigned it a potential of zero volts.

a. What would be the E^0 value for the $Br_2 + 2e^- \rightleftharpoons 2Br^-$ half-cell?
b. What would be the E^0 value for the $Al^{3+} + 3e^- \rightleftharpoons Al$ half-cell?
c. How much change would be observed in the E^0 value for the reaction involving $Br_2 + I^-$ using the I_2 half-cell as the standard?

22. If a strip of Ni were dipped into a solution of $AgNO_3$, what would be expected to occur? Explain, using E^0 values and equations.

23. a. What would happen if an aluminum spoon were used to stir a solution of $Zn(NO_3)_2$?
b. Could a strip of Zn be used to stir a solution of $Al(NO_3)_3$? Explain, using E^0 values.

24. How do the redox reactions for each of the following types of batteries differ?

a. zinc-carbon b. alkaline c. mercury

25. a. Why are some standard reduction potentials positive and some negative?
b. Compare the E^0 value for a metal with the reactivity of that metal.

MIXED REVIEW

26. Predict whether each of the following reactions will occur spontaneously as written by determining the E^0 value for potential reaction. Write and balance the overall equation for each reaction that does occur.

a. $Mg + Sn^{2+} \longrightarrow$
b. $K + Al^{3+} \longrightarrow$
c. $Li^{+} + Zn \longrightarrow$
d. $Cu + Cl_2 \longrightarrow$

27. Why is it possible for alkaline batteries to be smaller than zinc-carbon dry cells?

28. Draw a diagram of a voltaic cell whose two half-reactions consist of Ag in $AgNO_3$ and Ni in $NiSO_4$. Identify the anode and cathode, and indicate the directions in which the electrons and ions are moving.

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29. Identify the following reactions as redox or nonredox:

a. $Mg(s) + ZnCl_2(aq) \longrightarrow Zn(s) + MgCl_2(aq)$

b. $2H_2(g) + OF_2(g) \longrightarrow H_2O(g) + 2HF(g)$

c. $2KI(aq) + Pb(NO_3)_2(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$

d. $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$

e. $3CuCl_2(aq) + 2(NH_4)_3PO_4(aq) \longrightarrow 6NH_4Cl(aq) + Cu_3(PO_4)_2(s)$

f. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

30. Can a solution of $Sn(NO_3)_2$ be stored in an aluminum container? Explain, using E^0 values.

31. A voltaic cell is made up of a cadmium electrode in a solution of $CdSO_4$ and a zinc electrode in a solution of $ZnSO_4$. The two half-cells are separated by a porous barrier.

a. Which is the cathode, and which is the anode?

b. In which direction are the electrons flowing?

c. Write balanced equations for the two half-reactions, and write a net equation for the combined reaction.

32. Would the following pair of electrodes make a good battery? Explain.

$$Cd \longrightarrow Cd^{2+} + 2e^-$$
$$Fe \longrightarrow Fe^{2+} + 2e^-$$

33. Arrange the following in order of decreasing oxidation number of the nitrogen atom:
$N_2, NH_3, N_2O_4, N_2O, N_2H_4, NO_3^-$

34. Balance the following redox equations:

a. $SbCl_5 + KI \longrightarrow KCl + I_2 + SbCl_3$

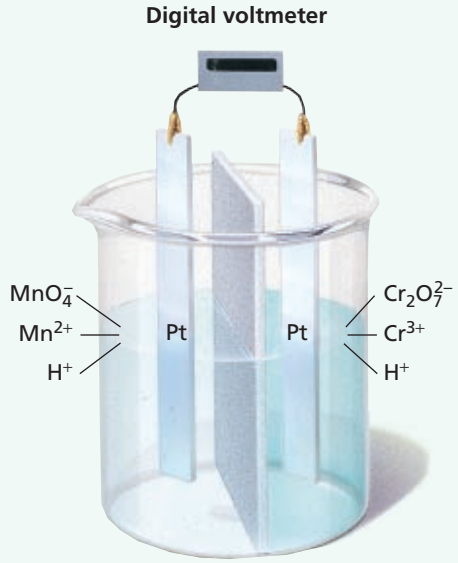
b. $Ca(OH)_2 + NaOH + ClO_2 + C \longrightarrow NaClO_2 + CaCO_3 + H_2O$

CRITICAL THINKING

35. Applying Models Explain how the oxidation-reduction chemistry of both the voltaic cell and the electrolytic cell are combined in the chemistry of rechargeable cells.

36. Applying Ideas In lead/acid batteries, such as your car battery, the degree of discharge of the battery can be determined by measuring the density of the battery fluid. Explain how this is possible.

37. Interpreting Graphics A voltaic cell is pictured below. Identify the species that is oxidized if current is allowed to flow.



TECHNOLOGY & LEARNING

38. Graphing Calculator: Calculate the Equilibrium Constant, Using the Standard Cell Voltage

The graphing calculator can run a program that calculates the equilibrium constant for an electrochemical cell using an equation called the Nernst equation, given the standard potential and the number of electrons transferred. Given that the standard potential is 2.041 V and that two electrons are transferred, you will calculate the equilibrium constant. The program will be used to make the calculations.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use.

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Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. What is the equilibrium constant when the standard potential is .099?
b. What is the equilibrium constant when the standard potential is 1.125?
c. What is the equilibrium constant when the standard potential is 2.500?

HANDBOOK SEARCH

39. Several reactions of aluminum are shown in the common reactions section for Group 13 of the *Elements Handbook*. Use these reactions to answer the following.
   a. Which of the five reactions shown are oxidation-reduction reactions? How do you know?
   b. For the redox reactions you listed for item a, identify what is oxidized and what is reduced.
   c. Write half-reactions for each equation you listed in item a.

40. Aluminum is described in Group 13 of the *Elements Handbook* as a self-protecting metal. This property of aluminum results from a redox reaction.
   a. Write the redox equation for the oxidation of aluminum.
   b. Write the half-reactions for this reaction showing the number of electrons transferred.
   c. What problems are associated with the buildup of aluminum oxide on electrical wiring made of aluminum?

RESEARCH & WRITING

41. Go to the library and find out what you can about the electroplating industry in the United States. What are the top three metals used for plating, and how many metric tons of each are used in the United States each year for electroplating?

42. Investigate the types of batteries being considered for electric cars. Write a report on the advantages and disadvantages of these types of batteries.

ALTERNATIVE ASSESSMENT

43. Performance Take an inventory of the types of batteries used in your home. Find out the voltage supplied by each battery and what electrochemical reaction each uses. Suggest why that electrochemical reaction is used in each case.

44. In our portable society, batteries have become a necessary power supply. As consumers, we want to purchase batteries that will last as long as possible. Advertisements tell us that some batteries last longer than others, but do they really? Design an investigation to answer the question. Is there a difference in longevity among the major brands of AA batteries? Add a cost-effectiveness component to your design.

45. When someone with a silver filling in a tooth bites down on an aluminum gum wrapper, saliva acts as an electrolyte. The system is an electrochemical cell which produces a small jolt of pain. Explain what occurs, using half-cell reactions and E° values.

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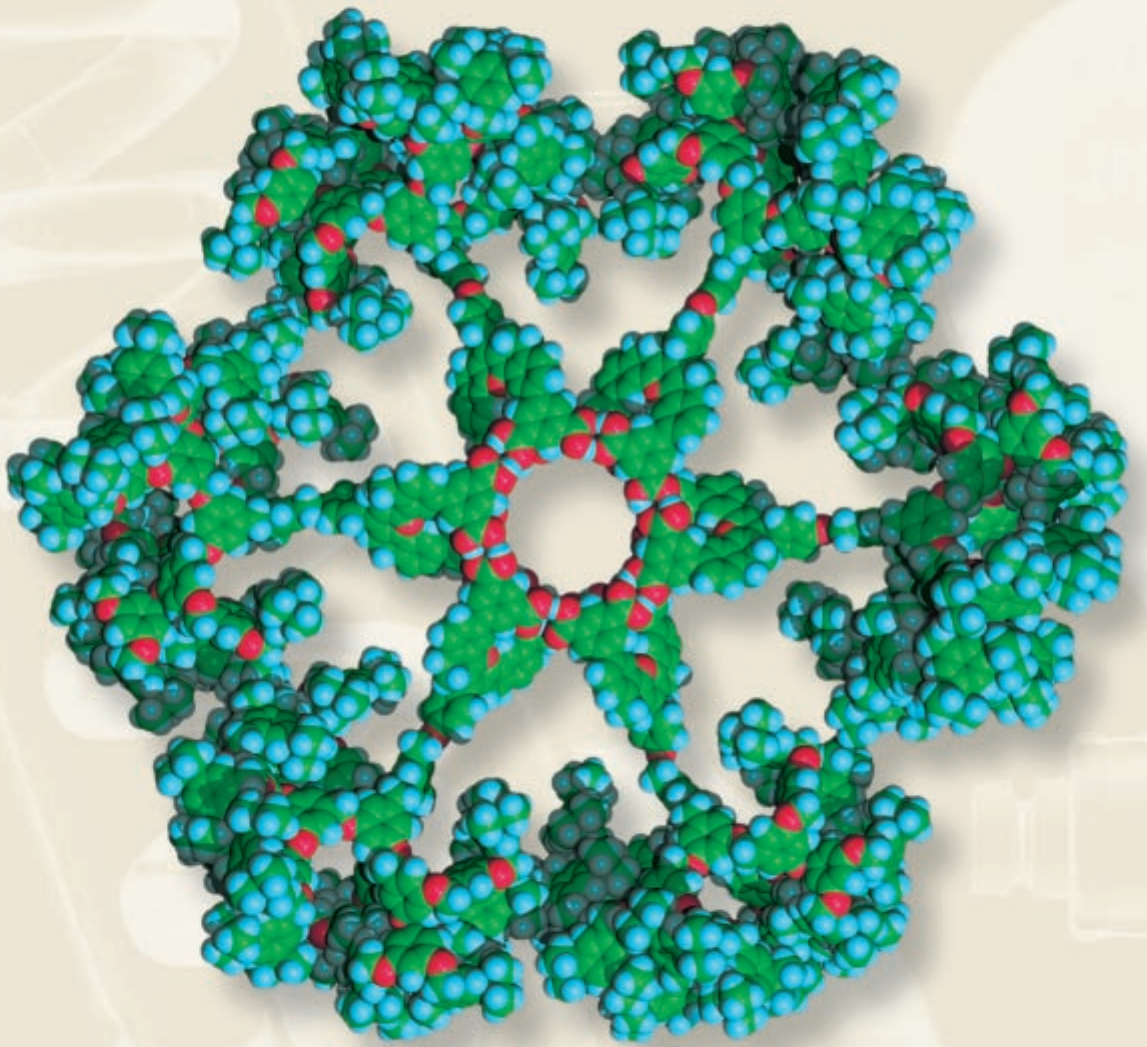
CHAPTER 20

Carbon and Hydrocarbons



Three-dimensional models help us visualize the shape of carbon compounds.

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Abundance and Importance of Carbon

SECTION 20-1

Objectives

- Relate the ability of a carbon atom to form covalent bonds to its atomic structure and hybrid orbitals.
- Identify the different allotropes of carbon and their structural differences.
- Explain how the different structures of carbon allotropes affect their properties.

Carbon is found in nature both as an element and in combined form. Although carbon ranks about 17th in abundance by mass among the elements in Earth's crust, it is exceedingly important because it is found in all living matter. Carbon is present in body tissues and in the foods you eat. It is also found in common fuels, such as coal, petroleum, natural gas, and wood.

Structure and Bonding of Carbon

Carbon, the first member of Group 14, has mostly nonmetallic properties. In its ground state, a carbon atom has an electronic configuration of $1s^2 2s^2 2p^2$. The two 1*s* electrons are tightly bound to the nucleus. The two 2*s* electrons and the two 2*p* electrons are the valence electrons. Carbon atoms show a very strong tendency to share electrons and form covalent bonds.

As was covered in Chapter 6, hybridization can be used to explain the bonding and geometry of most carbon compounds. Carbon atoms that form four single bonds have four sp^3 orbitals. These orbitals are directed toward the four corners of a regular tetrahedron, as shown in Figure 20-1. This results in the tetrahedral shape of methane, CH_4, and the zigzag pattern of molecules with multiple single-bonded carbon atoms, such as C_4H_{10}.

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Module 4: Chemical Bonding

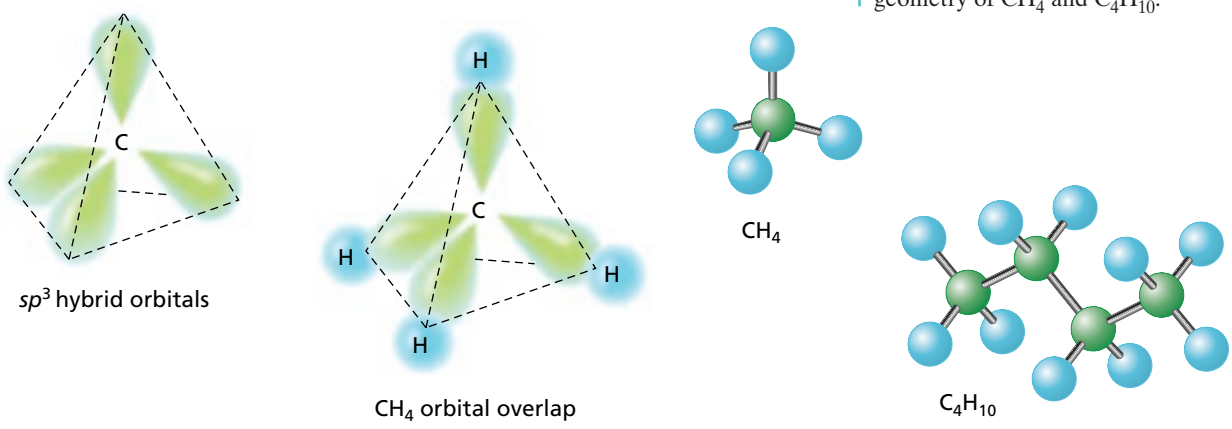

FIGURE 20-1 The orbital models show how the orientation of sp^3 hybrid orbitals relates to the geometry of CH_4 and C_4H_{10}.

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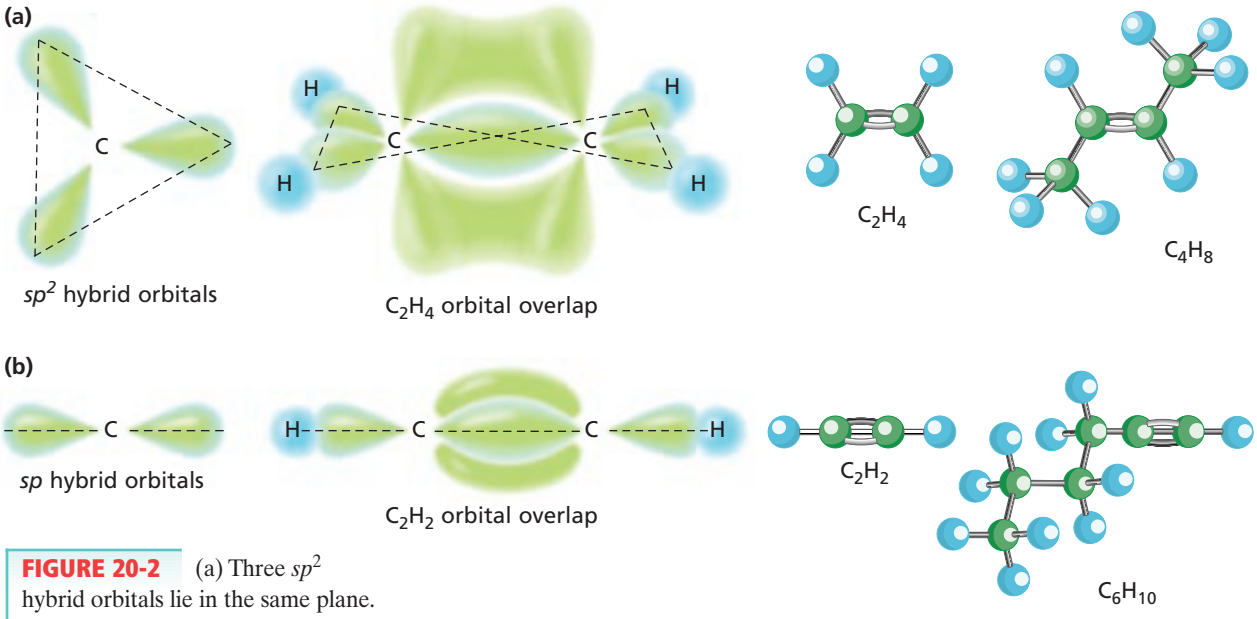

FIGURE 20-2 (a) Three sp^2 hybrid orbitals lie in the same plane. The C_2H_4 orbital overlap model shows the orientation of sp^2 hybrid orbitals in molecules that contain a double bond, such as C_2H_4 and C_4H_8. (b) The C_2H_2 orbital overlap model shows the orientation of *sp* hybrid orbitals in molecules that contain a triple bond, such as C_2H_2 and C_6H_{10}.

Carbon atoms form double bonds through sp^2 hybridization, as shown in Figure 20-2(a). When carbon atoms form double bonds, the sp^2 hybrid orbitals of both carbon atoms lie in the same plane, as shown in the orbital overlap model of ethene, C_2H_4. Because the hydrogen atoms of C_2H_4 also bond with carbon sp^2 orbitals, all six atoms lie in the same plane. The three-dimensional models of C_2H_4 and C_4H_8 show the geometry of molecules containing carbon-carbon double bonds.

Carbon triple bonds are linear due to the linear arrangement of two *sp* hybrid orbitals, as shown in Figure 20-2(b). This can be seen in the orbital overlap model for ethyne, C_2H_2. The three-dimensional models of C_2H_2 and C_6H_{10} show the geometry of molecules containing carbon-carbon triple bonds.

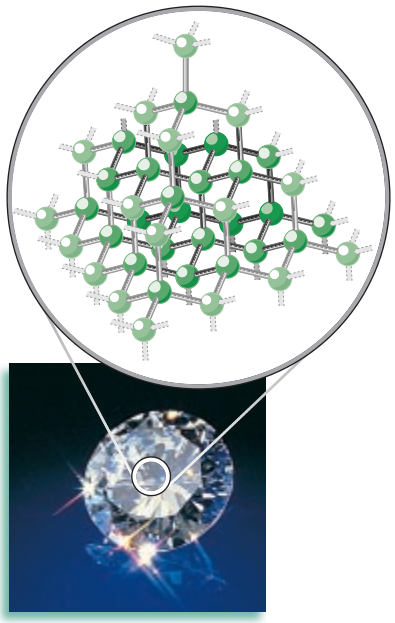

FIGURE 20-3 In diamond, the carbon atoms are densely packed because each carbon atom is bonded to four tetrahedrally oriented carbon atoms.

Allotropes of Carbon

Carbon occurs in several solid allotropic forms that have dramatically different properties. **Diamond** *is a colorless, crystalline, solid form of carbon.* **Graphite** *is a soft, black, crystalline form of carbon that is a fair conductor of electricity.* **Fullerenes** *are dark-colored solids made of spherically networked carbon-atom cages.*

Diamond

Diamond is the hardest material known. It is the most dense form of carbon—about 3.5 times more dense than water. It also has an extremely high melting point (greater than 3500°C). These properties of diamond can be explained by its structure. The model in Figure 20-3 shows carbon atoms in diamond bonded covalently in a network fashion. Each

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carbon atom is tetrahedrally oriented to its four nearest neighbors. The distance between the carbon-atom nuclei has been measured to be 154 pm. Because of diamond's extreme hardness and high melting point, its major industrial uses are for cutting, drilling, and grinding. Diamonds used in industry are not of gem quality.

Another property of diamond is its ability to conduct heat. A diamond crystal conducts heat more than five times more readily than silver or copper, which are the best metallic conductors. In diamond, heat is conducted by the transfer of energy of vibration from one carbon atom to the next. In a diamond crystal, this process is very efficient because the carbon atoms have a small mass. The forces holding the atoms together are strong and can easily transfer vibratory motion among the atoms. However, unlike metals, diamond does not conduct electricity. Because all the valence electrons are used in forming localized covalent bonds, none of the electrons can migrate.

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Graphite

Graphite is nearly as remarkable for its softness as diamond is for its hardness. It feels greasy and crumbles easily, characteristics that are readily explained by its structure. The carbon atoms in graphite are arranged in layers that form thin hexagonal plates, as shown by the model in Figure 20-4.

The distance between the nuclei of adjacent carbon atoms within a layer has been measured to be 142 pm. This distance is less than the distance between adjacent carbon atom nuclei in diamond. However, the distance between the nuclei of atoms in adjacent layers measures 335 pm. Because the average distance between carbon atoms in graphite is greater than the average distance in diamond, graphite has a lower density.

The layers of carbon atoms in graphite are too far apart to be held together by covalent bonds. Only weak London dispersion forces hold the layers together. Because of the weak attraction, the layers can slide across one another. This property allows graphite to be used as a lubricant and in pencil "lead."

Within each layer, each carbon atom is bonded to only three other carbon atoms. These bonds are examples of resonance hybrid bonds, which were discussed in Chapter 6. The bonding electrons of resonance hybrid bonds can be thought of as delocalized. **Delocalized electrons** *are electrons shared by more than two atoms*.

Graphite is a fairly good conductor of electricity, even though it is a nonmetal, because the delocalized electrons move freely within each layer. Like diamond, graphite has a high melting point (3652°C). This is because the structure created by delocalized electrons results in a strongly bonded covalent network. Another use of graphite is in graphite fibers. Graphite fibers are stronger and stiffer than steel, but less dense. The strength of the bonds within a layer makes graphite difficult to pull apart in the direction parallel to the surface of the layers. The strength and light weight of graphite fiber have led to its use in products such as sporting goods and aircraft.

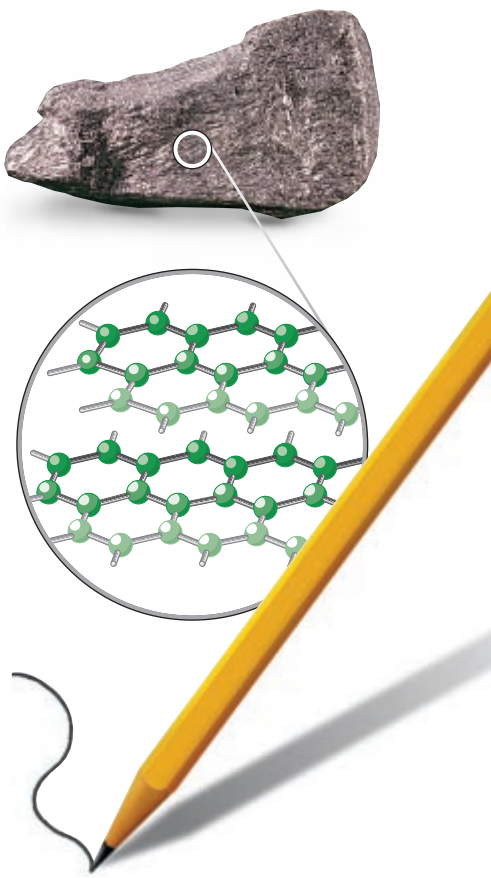

FIGURE 20-4 Notice the space between layers in the ball-and-stick model of graphite. Graphite pencils mark on paper because adjacent layers can slide past each other.

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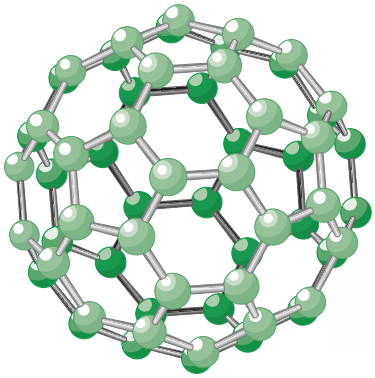
(a)



(b)

(c)

FIGURE 20-5 (a) Buckminsterfullerene was named after Buckminster Fuller, who invented geodesic domes like the one shown here. (b) The structure of buckminsterfullerene resembles the pattern of a soccer ball (c).

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Fullerenes

In the mid-1980s a new allotropic form of carbon was discovered. The 1996 Nobel Prize in chemistry was awarded to Richard E. Smalley, Robert F. Curl, and Harold W. Kroto, leaders of the research teams that discovered this class of compounds, fullerenes.

Fullerenes are part of the soot that forms when carbon-containing materials are burned with limited oxygen. Their structures consist of near-spherical cages of carbon atoms. The most stable of these is C_{60}, shown in Figure 20-5. C_{60} is formed by 60 carbon atoms arranged in interconnected five- and six-membered rings.

Because of its structural resemblance to geodesic domes, Richard Smalley and his co-workers at Rice University named C_{60} "buckminsterfullerene" in honor of the geodesic-dome architect, Buckminster Fuller. The whole family of carbon-atom cages, which have a wide range in the number of carbon atoms, are therefore called fullerenes. Because the structure of C_{60} also resembles the design of a soccer ball, C_{60} is also known less formally as buckyball. Scientists are currently trying to find practical uses for these substances.

SECTION REVIEW

1. What makes carbon an important element in the study of chemistry?
2. What type of hybrid orbital is found in carbon double bonds? In carbon triple bonds?
3. How does the structure of graphite relate to its properties and uses?
4. a. How are the structures of different fullerenes similar?
   b. How do they differ?

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Organic Compounds

SECTION 20-2

Objectives

- Explain how the structure and bonding of carbon lead to the diversity and number of organic compounds.
- Explain the importance and limitations of molecular and structural formulas.
- Compare structural and geometric isomers.

All organic compounds contain carbon atoms. However, not all carbon-containing compounds are classified as organic. There are a few exceptions, such as Na_2CO_3, CO, and CO_2, that are considered inorganic. **Organic compounds,** then, can be defined as *covalently bonded compounds containing carbon, excluding carbonates and oxides*. Figure 20-6 shows a few familiar items that contain organic compounds.

Carbon Bonding and the Diversity of Organic Compounds

The diversity of organic compounds results from the uniqueness of carbon's structure and bonding. Carbon's electronic structure allows it to bind to itself to form chains and rings, to bind covalently to other elements, and to bind to itself and other elements in different arrangements.

FIGURE 20-6 Aspirin, polyethylene in plastic bags, citric acid in fruit, and amino acids in animals are all examples of organic compounds.

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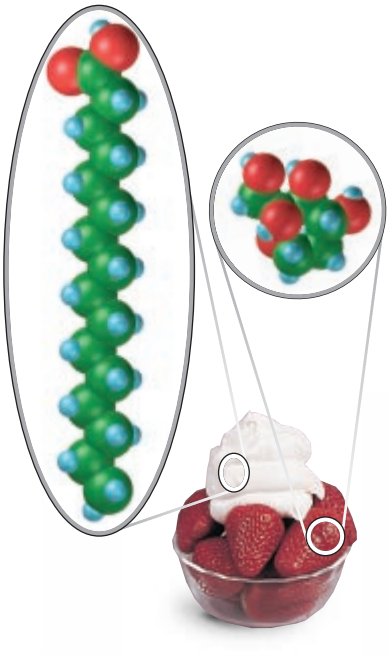


FIGURE 20-7 Compare the shape of a fatty acid found in cream with that of fructose, found in fruit. In the fatty acid, the carbon atoms are in chains. In fructose, carbon atoms form a ring.

Carbon-Carbon Bonding

Carbon atoms are unique in their ability to form long chains and rings of covalently bonded atoms. This type of bonding is known as **catenation,** *the covalent binding of an element to itself to form chains or rings*. This produces a multitude of chain, branched-chain, and ring structures. In addition, carbon atoms in these structures can be linked by single, double, or triple covalent bonds. Examples of molecules containing carbon-atom rings and chains are shown in Figure 20-7.

Carbon Bonding to Other Elements

Besides binding to other carbon atoms, carbon atoms bind readily to elements with similar electronegativities. Organic compounds consist of carbon and these other elements. **Hydrocarbons** *are composed of only carbon and hydrogen; they are the simplest organic compounds.* Other organic compounds contain hydrocarbon backbones to which other elements, primarily O, N, S, and the halogens, are attached. Figure 20-8 shows a molecule in which carbon atoms are bound to other elements.

Arrangement of Atoms

The bonding capabilities of carbon also allow for different arrangements of atoms. This means that some compounds may contain the same atoms but have different properties because the atoms are arranged differently. For example, the molecular formula C_2H_6O represents both ethanol and dimethyl ether. *Compounds that have the same molecular formula but different structures are called* **isomers.** As the number of carbon atoms in a molecular formula increases, the number of possible isomers increases rapidly. For example, there are 18 isomers with the molecular formula C_8H_{18}, 35 with the molecular formula C_9H_{20}, and 75 with the molecular formula $C_{10}H_{22}$. For the molecular formula of just 40 carbon atoms and 82 hydrogen atoms, $C_{40}H_{82}$, there are theoretically 69 491 178 805 831 isomers. To distinguish one from another, more information than just the molecular formula is needed.

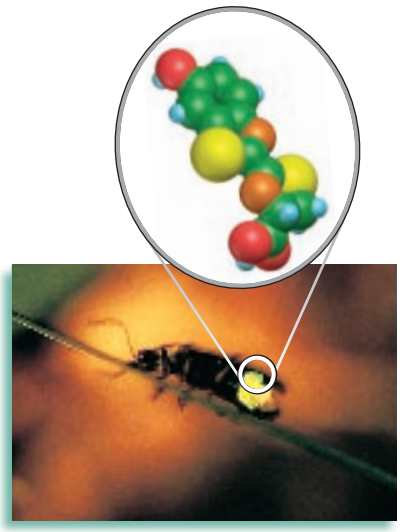
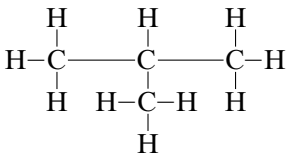


FIGURE 20-8 In firefly luciferin, carbon atoms bind to hydrogen, oxygen, nitrogen, and sulfur. Luciferin is responsible for the light emitted from the tail of a firefly.

Structural Formulas

For this reason, organic chemists use structural formulas to represent organic compounds. *A* **structural formula** *indicates the number and types of atoms present in a molecule and also shows the bonding arrangement of the atoms.* For example, one possible structural formula for an isomer of C_4H_{10} is the following.



Structural formulas are sometimes condensed to make them easier to read. In one type of condensed structure, hydrogen single covalent bonds are not shown. The hydrogen atoms are understood to bind to the

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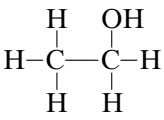
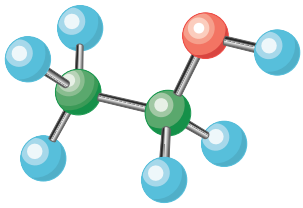
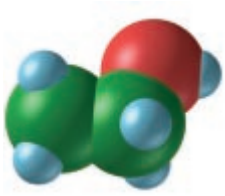




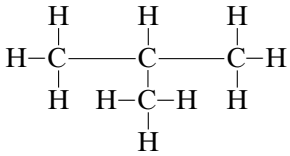
Ball-and-stick model



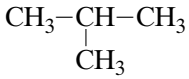
Space-filling model

FIGURE 20-9 The structure of ethanol can be represented in different ways. Ball-and-stick and space-filling models represent the three-dimensional shape of the molecule.

atom they are written beside. The following structural and condensed structural formulas represent the same molecule.



is the same as



Remember that the structural formula does not accurately show the three-dimensional shape of the molecule. Three-dimensional shape is depicted with drawings or models, as shown for ethanol in Figure 20-9.

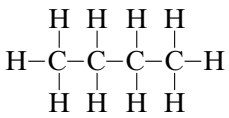
As you continue your study, you may find that the use of dashes can be eliminated by writing in a horizontal row the symbols and subscripts for the groups of carbon and hydrogen atoms that appear in a molecule. For example, ethane is written as CH_3CH_3 and propane as $CH_3CH_2CH_3$.

Isomers

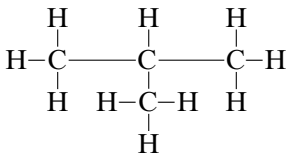
You have learned that isomers are compounds that have the same molecular formula but different structural formulas. Isomers can be further classified by structure and geometry.

Structural Isomers

Structural isomers *are isomers in which the atoms are bonded together in different orders.* For example, the atoms of the molecular formula C_4H_{10} can be arranged in two different ways.



butane



methylpropane

Notice that the formula for butane shows a continuous chain of four carbon atoms. The chain may be bent or twisted, but it is continuous. The formula of methylpropane shows a continuous chain of three carbon atoms, with the fourth carbon atom attached to the second carbon atom of the chain.

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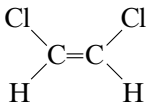
TABLE 20-1 ***Physical Properties of the Structural Isomers Butane and Methylpropane***

	Melting point (°C)	Boiling point (°C)	Density at 20°C (g/mL)
butane	–138.4	–0.5	0.5788
methylpropane	–159.4	–11.633	0.549

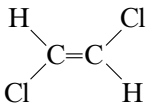
Structural isomers can have different physical or chemical properties. For example, butane and methylpropane have different melting points, boiling points, and densities, as shown in Table 20-1.

Geometric Isomers

Geometric isomers *are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different.* Consider the molecule 1,2-dichloroethene, which contains a double bond. The double bond prevents free rotation and holds groups to either side of the molecule. This means there can be two different 1,2-dichloroethene geometric isomers as shown below.



cis

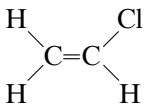


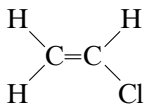
trans

Because the two chlorine atoms are on the same side of the molecule in the first structure, it is called *cis*. In the second molecule, the two chlorine atoms are on opposite sides of the molecule, and so the molecule is called *trans*. Notice that in both molecules the bonding order of the atoms is the same: each carbon atom in the double bond is also bound to one chlorine atom and one hydrogen atom.

Now consider the molecule 1,2-dichloroethane. Atoms attached to the carbon atoms can rotate freely around the single carbon-carbon bond, as shown in Figure 20-10. There are no geometric isomers of 1,2-dichloroethane. *In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond.*

Now consider two apparent structures for another molecule with a double bond, chloroethene.





Although these structures may appear different at first glance, they are actually the same. In *both* structures, two hydrogen atoms are on one side of the molecule, and one chlorine atom and one hydrogen atom are on the other. *A molecule can have a geometric isomer only if two carbon atoms in a rigid structure each have two different groups attached.*

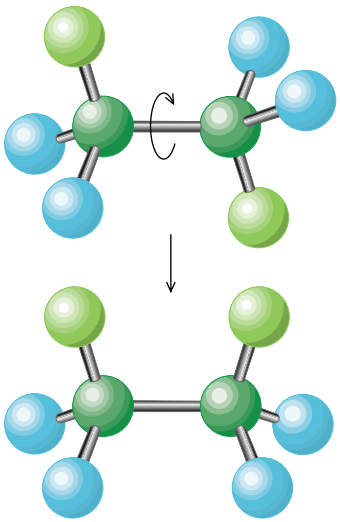


FIGURE 20-10 Unlike double bonds, single bonds allow free rotation within a molecule. Groups attached to the carbon atoms are not held to one side of the molecule, so there are no geometric isomers.

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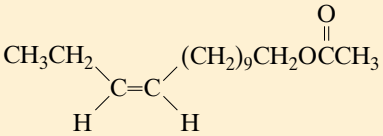
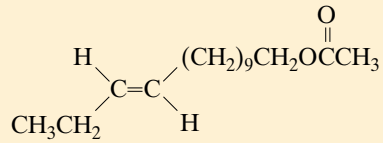


cis-11-tetradecenyl acetate



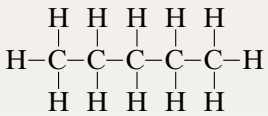
trans-11-tetradecenyl acetate

FIGURE 20-11 Males of the Iowa strain of the European corn borer respond most strongly to mixtures of the female sex attractant pheromone that are 96% *cis* isomer. But males of the New York strain respond most strongly to mixtures containing 97% *trans* isomer.

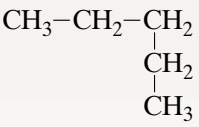
Like structural isomers, geometric isomers differ in physical and chemical properties. Some geometric isomers are known to differ in physiological behavior as well. For example, insects can communicate by chemicals called pheromones and may distinguish between the geometric isomers of pheromones. One geometric isomer of a pheromone may be physiologically active, while the other will be only slightly active or not at all. The European corn borer, shown in Figure 20-11, distinguishes between isomers of its sex-attractant pheromone. Another example of differences between geometric isomers is found in fatty acids. Natural unsaturated fatty acids are primarily *cis*-fatty acids. Hydrogenation is used to convert vegetable oil, which contains unsaturated fatty acids, into a solid fat, such as margarine or vegetable shortening. During hydrogenation *trans*-fatty acids are produced. Research has shown that there may be health risks associated with diets high in *trans*-fatty acids.

SECTION REVIEW

1. What are three characteristics of carbon that contribute to the diversity of organic compounds?
2. Define the term *isomer,* and distinguish between structural and geometric isomers.
3. Which of the following types of molecular representations can be used to show differences between isomers? Explain why each can or cannot.
   a. molecular formula
   b. structural formula
   c. three-dimensional drawing or model
4. Write the formula for methylpropane (shown at the right on page 631) in a horizontal row.
5. Which of the following can represent the same molecule?

   a. 

   b. $CH_3-CH_2-CH_2-CH_3$

   c. 

   d. C_5H_{12}

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SECTION 20-3

OBJECTIVES

- Recognize the important structural feature of saturated hydrocarbons, alkanes.
- Be able to name and write structural formulas for alkanes.
- Explain how structures of alkanes relate to their properties and how those properties affect the uses of specific alkanes.

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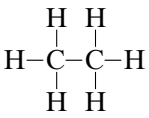
Saturated Hydrocarbons

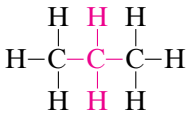
Hydrocarbons are grouped mainly by the type of bonding between carbon atoms. **Saturated hydrocarbons** *are hydrocarbons in which each carbon atom in the molecule forms four single covalent bonds with other atoms.*

Alkanes

Hydrocarbons that contain only single bonds are **alkanes.** In Table 20-2, the molecular formulas, structural formulas, and space-filling models are given for alkanes with one to four carbon atoms. If you examine the molecular formulas for successive alkanes in Table 20-2, you will see a clear pattern. Each member of the series differs from the preceding one by one carbon atom and two hydrogen atoms. For example, propane, C_3H_8, differs from ethane, C_2H_6, by one carbon atom and two hydrogen atoms, a $-CH_2-$ group.



ethane



propane

Compounds that differ in this fashion belong to a homologous series. A **homologous series** *is one in which adjacent members differ by a constant unit.* It is not necessary to remember the molecular formulas for all members of a homologous series. Instead, a general molecular formula can be used to determine the formulas. Look at the molecular formulas for ethane and propane, C_2H_6 and C_3H_8. They both fit the formula C_nH_{2n+2}. For ethane, $n = 2$, so there are two carbon atoms and $(2 \times 2) + 2 = 6$ hydrogen atoms. For propane, $n = 3$, so there are three carbon atoms and $(2 \times 3) + 2 = 8$ hydrogen atoms. Now consider a molecule for which we do not know the molecular formula. Suppose a member of this series has 30 carbon atoms in its molecules. Then $n = 30$, and there are $(2 \times 30) + 2 = 62$ hydrogen atoms. The formula is $C_{30}H_{62}$.

Notice that for alkanes with three or fewer carbon atoms, only one molecular structure is possible. However, in alkanes with more than three carbon atoms, the chains can be straight or branched. Thus,

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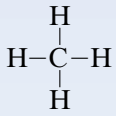
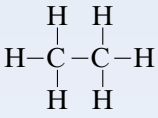
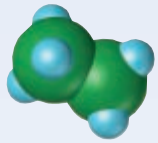
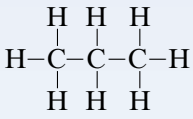
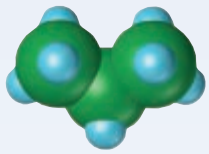
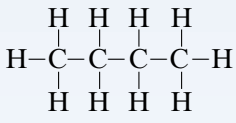
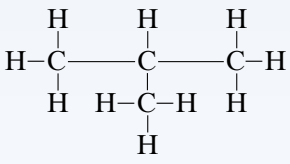
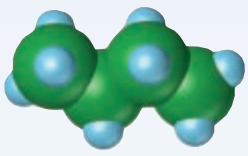
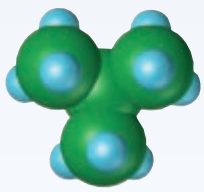
TABLE 20-2 *Alkanes with One to Four Carbon Atoms*

Molecular formulas	Structural formulas	Space-filling models
CH_4	 methane	
C_2H_6	 ethane	
C_3H_8	 propane	
C_4H_{10}	 butane  methylpropane	 

alkanes with four or more carbon atoms have structural isomers. There are two possible structural isomers for alkanes with four carbon atoms, butane and methylpropane.

Cycloalkanes

Cycloalkanes *are alkanes in which the carbon atoms are arranged in a ring, or cyclic, structure.* The structural formulas for cycloalkanes are often drawn in a simplified form. It is understood that there is a carbon

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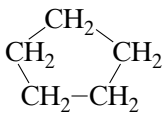
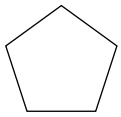
atom at each corner and enough hydrogen atoms to complete the four bonds to each carbon atom.



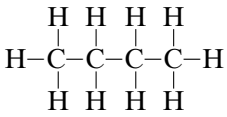
cyclopentane

or

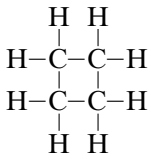


cyclopentane

Because there are no free ends where a carbon atom is attached to three hydrogen atoms, there are two fewer hydrogen atoms in cycloalkanes than in noncyclic alkanes.



butane
C_4H_{10}



cyclobutane
C_4H_8

The general structure for cycloalkanes, C_nH_{2n}, shows that they have $2 \times n$ hydrogen atoms. This is two fewer hydrogen atoms than noncyclic alkanes, C_nH_{2n+2}, which have $(2 \times n) + 2$ hydrogen atoms.

Systematic Names of Alkanes

Historically, the names of many organic compounds were derived from the sources in which they were found. As more organic compounds were discovered, a systematic naming method became necessary. The systematic method used primarily in this book was developed by the International Union of Pure and Applied Chemistry, IUPAC.

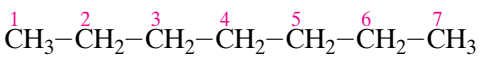
The basic part of the systematic name of an organic compound is the name of the longest carbon chain, or parent hydrocarbon, in the molecule. Table 20-3 gives the names of the prefixes for carbon-atom chains up to 10 carbon atoms long. Beginning with *pent-*, the prefixes are Greek or Latin numerical prefixes.

TABLE 20-3 *Carbon-Atom Chain Prefixes*

Number of carbon atoms	Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-

Unbranched-Chain Alkane Nomenclature

To name an unbranched alkane, find the prefix in Table 20-3 that corresponds to the number of carbon atoms in the chain of the hydrocarbon. Then add the suffix *-ane* to the prefix. An example is shown below.



heptane

The molecule has a chain seven carbon atoms long, so the prefix *hept-* is added to the suffix *-ane* to form *heptane*.

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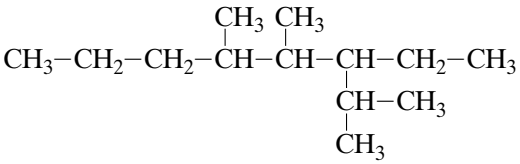
TABLE 20-4 Some Straight-Chain Alkyl Groups

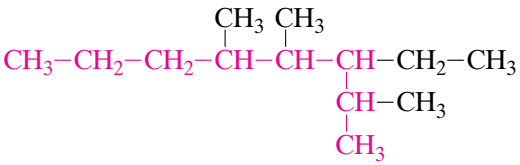
Alkane	Name	Alkyl group	Name
CH_4	methane	$-CH_3$	methyl
CH_3-CH_3	ethane	$-CH_2-CH_3$	ethyl
$CH_3-CH_2-CH_3$	propane	$-CH_2-CH_2-CH_3$	propyl
$CH_3-CH_2-CH_2-CH_3$	butane	$-CH_2-CH_2-CH_2-CH_3$	butyl
$CH_3-CH_2-CH_2-CH_2-CH_3$	pentane	$-CH_2-CH_2-CH_2-CH_2-CH_3$	pentyl

Branched-Chain Alkane Nomenclature

The naming of branched-chain alkanes also follows a systematic method. The hydrocarbon branches of alkanes are alkyl groups. **Alkyl groups** *are groups of atoms that are formed when one hydrogen atom is removed from an alkane molecule*. Alkyl groups are named by replacing the suffix *-ane* of the parent alkane with the suffix *-yl*. Some examples are shown in Table 20-4. Alkyl group names are used when naming branched-chain alkanes. We will only present the method for naming simple branched-chain alkanes with only straight-chain alkyl groups. Consider the following molecule.



To name this molecule, locate the parent hydrocarbon. The parent hydrocarbon is the longest continuous chain that contains the most straight-chain branches. In this molecule, there are two chains that are eight carbon atoms long. The parent hydrocarbon is the chain that contains the most straight-chain branches. Do not be tricked by the way the molecule is drawn. The longest chain may be shown bent.



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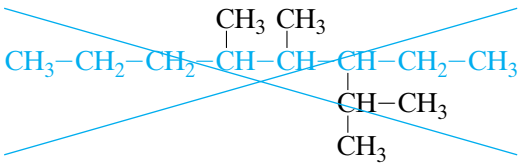

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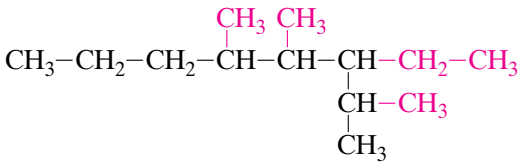
To name the parent hydrocarbon, add the suffix *-ane* to the prefix *oct-* (for a carbon-atom chain with eight carbon atoms) to form *octane.* Now identify and name the alkyl groups.



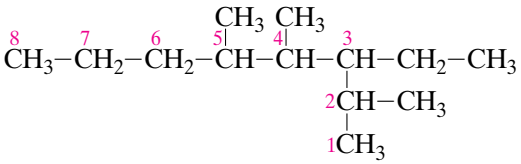
The three $-CH_3$ groups are methyl groups. The $-CH_2-CH_3$ group is an ethyl group. Arrange the names in alphabetical order in front of the name of the parent hydrocarbon.

ethyl methyloctane

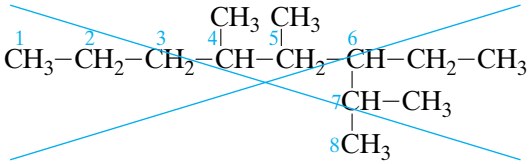
To show that there are three methyl groups present, attach the prefix *tri-* to the name *methyl* to form *trimethyl*.

ethyl **tri**methyloctane

Now we need to show the locations of the alkyl groups on the parent hydrocarbon. Number the octane chain so that the alkyl groups have the lowest numbers possible.



NOT



Place the location numbers of *each* of the alkyl groups in front of its name. Separate the numbers from the names of the alkyl groups with hyphens. The ethyl group is on carbon *3*.

3-ethyl trimethyloctane

Because there are three methyl groups, there will be three numbers, separated by commas, in front of *trimethyl*.

3-ethyl**-2,4,5-**trimethyloctane

The full name is 3-ethyl-2,4,5-trimethyloctane.

The procedure for naming simple branched-chain alkanes can be summarized as follows.

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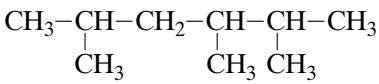
Alkane Nomenclature

1. **Name the parent hydrocarbon.** Find the longest continuous chain of carbon atoms with straight-chain branches. Add the suffix *-ane* to the prefix corresponding to the number of carbon atoms in the chain.
2. **Add the names of the alkyl groups.** Add the names of the alkyl groups in front of the name of the parent hydrocarbon in alphabetical order. When there is more than one branch of the same alkyl group present, attach the appropriate numerical prefix to the name, *di* = 2, *tri* = 3, *tetra* = 4, and so on. Do this after the names have been put in alphabetical order.
3. **Number the carbon atoms in the parent hydrocarbon.** If one or more alkyl groups are present, number the carbon atoms in the continuous chain to give the lowest numbers possible in the name. If there are two equivalent lowest positions with two different alkyl groups, give the lowest number to the alkyl group that comes first in the name. (This will be the alkyl group that is first in alphabetical order, *before* any prefixes are attached.)
4. **Insert position numbers.** Put the position numbers of each alkyl group in front of the name of that alkyl group.
5. **Punctuate the name.** Separate the position numbers from the names with hyphens. If there are more than one number in front of a name, separate the numbers by commas.

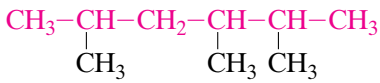
SAMPLE PROBLEM 20-1

Name the following simple branched-chain alkane:



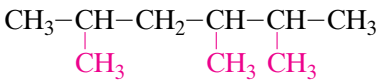
SOLUTION

1. Identify and name the parent hydrocarbon.



Because the longest continuous chain contains six carbon atoms, the parent hydrocarbon is *hexane*.

2. Identify and name the alkyl groups attached to the chain.



There is only one type of alkyl group, with one carbon atom. Alkyl groups with one carbon atom are methyl groups. Add the name *methyl* in front of the name of the continuous chain. Add the prefix *tri-* to show that there are three methyl groups present.

trimethylhexane

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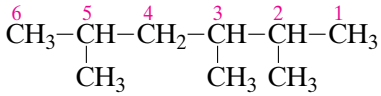
3. Number the carbon atoms in the continuous chain so that the alkyl groups have the lowest numbers possible.



4. The methyl groups are on the carbon atoms numbered *2*, *3*, and *5*. Put the numbers of the positions of the alkyl groups, separated by commas, in front of the name of the alkyl group. Separate the numbers from the name with a hyphen.

2,3,5-trimethylhexane

The complete name is 2,3,5-trimethylhexane.

SAMPLE PROBLEM 20-2

Draw the condensed structural formula of 3-ethyl-4-methylhexane.

SOLUTION

1. Identify the name of the parent hydrocarbon.

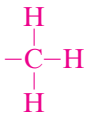
3-ethyl-4-methyl**hexane**

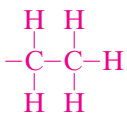
The parent hydrocarbon is hexane, so there are six carbon atoms in the chain. Draw and number the carbon atoms in the chain.

2. Identify the alkyl groups, and determine the number of carbon atoms in the alkyl groups.

3-**ethyl**-4-**methyl**hexane

Methyl groups have one carbon atom and ethyl groups have two carbon atoms.

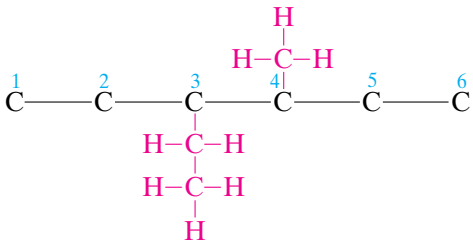




3. Locate the position numbers for the ethyl and methyl groups.

3-ethyl-**4**-methylhexane

Draw the alkyl groups on the parent hydrocarbon in the correct positions.



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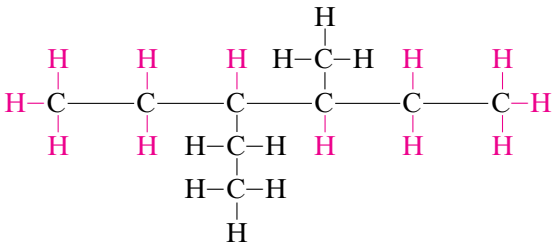
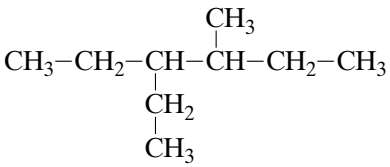
Notice that in this molecule the methyl group and the ethyl group were in equivalent positions from the end of the chain. They are both on third carbons from the end. In such a case, the alkyl group that comes first in the name is given the lower number.

4. Add the correct number of hydrogen atoms so that each carbon atom has four single bonds. This is the complete, uncondensed, structural formula.

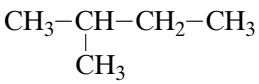


5. To draw the condensed structural formula, show only the bonds between carbon atoms.



PRACTICE

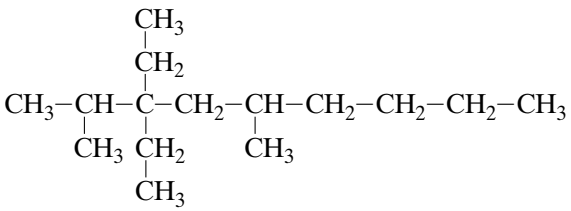
1. Name the following molecule:



Answer
methylbutane

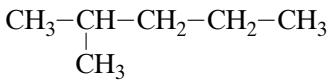
2. Draw the condensed structural formula for 3,3-diethyl-2,5-dimethylnonane.

Answer

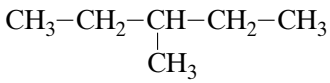


3. Draw the condensed structural formulas for the two structural isomers of methylpentane and name the isomers.

Answer



2-methylpentane



3-methylpentane

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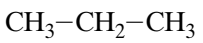
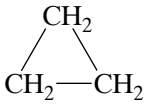
Cycloalkane Nomenclature

When naming simple cycloalkanes, the cycloalkane is the parent hydrocarbon. Cycloalkanes are named by adding the prefix *cyclo-* to the name of the straight-chain alkane with the same number of hydrocarbons.

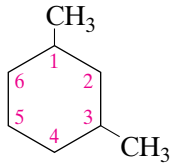


propane



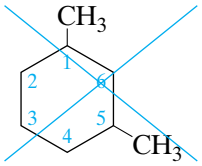
cyclopropane

When there is only one alkyl group attached to the ring, no position number is necessary. When there is more than one alkyl group attached to the ring, the carbon atoms in the ring are numbered to give the lowest numbers possible to the alkyl groups. This means that one of the alkyl groups will always be in position 1.



1,3-dimethylcyclohexane

NOT



~~1,5-dimethylcyclohexane~~

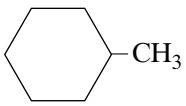
The rules for naming cycloalkanes can be summarized as follows.

Cycloalkane Nomenclature

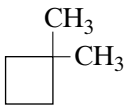
Use the rules for alkane nomenclature on page 639, with the following exceptions.

1. **Name the parent hydrocarbon.** Count the number of carbon atoms in the ring. Add the prefix *cyclo-* to the name of the corresponding straight-chain alkane.
2. **Add the names of the alkyl groups.**
3. **Number the carbon atoms in the parent hydrocarbon.** If there are two or more alkyl groups attached to the ring, number the carbon atoms in the ring. Assign position number one to the alkyl group that comes first in alphabetical order. Then, number in the direction that gives the next lowest number.
4. **Insert position numbers.**
5. **Punctuate the name.**

Two examples of correctly named cycloalkanes are given below.



methylcyclohexane



1,1-dimethylcyclobutane

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TABLE 20-5 Properties of Straight-Chain Alkanes

Molecular formula	IUPAC name	Boiling point (°C)	State at room temperature
CH_4	methane	–164	gas
C_2H_6	ethane	–88.6	
C_3H_8	propane	–42.1	
C_4H_{10}	butane	–0.5	
C_5H_{12}	pentane	36.1	liquid
C_8H_{18}	octane	125.7	
$C_{10}H_{22}$	decane	174.1	
$C_{17}H_{36}$	heptadecane	301.8	solid
$C_{20}H_{42}$	eicosane	343	

Properties and Uses of Alkanes

Properties for some straight-chain alkanes are listed in Table 20-5. The trends in these properties can be explained by examining the structure of alkanes. The carbon-hydrogen bonds of alkanes are nonpolar. The only forces of attraction between nonpolar molecules are weak intermolecular forces, or London dispersion forces. The strength of London dispersion forces increases as the mass of a molecule increases.

Physical States

The physical states at which some alkanes exist at room temperature and atmospheric pressure are found in Table 20-5. Alkanes with the lowest molecular mass, those with one to four carbon atoms, are gases. **Natural gas** *is a fossil fuel composed primarily of alkanes containing one to four carbon atoms*. The existence of these alkanes as gases agrees with the idea that very small molecules have weak London dispersion forces between them and are not held together tightly. Larger alkanes are liquids. Gasoline and kerosene consist mostly of liquid alkanes. Stronger London dispersion forces hold these molecules close enough together to form liquids. Alkanes with a very high molecular mass are solids, corresponding to a greater increase in London dispersion forces. Paraffin wax contains solid alkanes. It can be used in candles, as shown in Figure 20-12.

FIGURE 20-12 Paraffin wax, used in candles, contains solid alkanes. Molecules of paraffin wax contain 26 to 30 carbon atoms.

Boiling Points

The boiling points of alkanes, also shown in Table 20-5, increase with increasing molecular mass. As London dispersion forces increase, more energy, or heat, is required to pull the molecules apart. This property is used in the separation of petroleum, a major source of alkanes. **Petroleum** *is a complex mixture of different hydrocarbons that varies greatly in composition.* The hydrocarbon molecules in petroleum contain from one to more than fifty carbon atoms. This range allows the separation of

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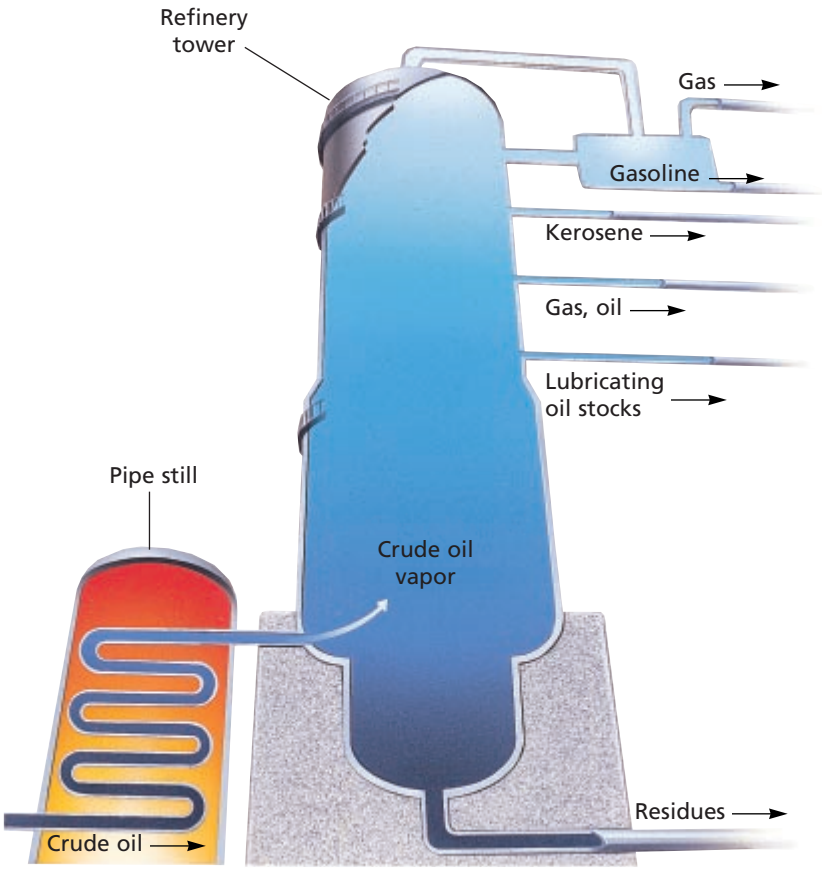
TABLE 20-6 *Petroleum Fractions*

Fraction	Size range of molecules	Boiling-point range (°C)
Gasoline	C_4–C_{12}	up to 200
Kerosene	C_{10}–C_{14}	180–290
Middle distillate, such as heating oil, gas-turbine fuel, diesel	C_{12}–C_{20}	185–345
Wide-cut gas oil, such as lubricating oil, waxes	C_{20}–C_{36}	345–540
Asphalt	above C_{36}	residues

petroleum into different portions with different boiling point ranges, as shown in Table 20-6. In **fractional distillation,** shown in Figure 20-13, *components of a mixture are separated on the basis of boiling point, by condensation of vapor in a fractionating column*. During its fractional distillation, petroleum is heated to about 370°C. Nearly all the components of the petroleum are vaporized at this temperature. As the vapors rise in the fractionating column, or tower, they are gradually cooled.

FIGURE 20-13 (a) Fractional distillation takes place in petroleum refinery towers. (b) This is a model of a fractional distillation tower. Because fractions contain hydrocarbons of different masses, they condense and are drawn off at different levels.

(a)



(b)

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Alkanes with higher boiling points have higher condensation temperatures and condense for collection lower in the tower. For example, lubricating oils, which have higher condensation temperatures than gasoline has, are collected lower in the fractionating tower.

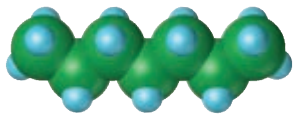
Combustion

Alkanes are less reactive than other hydrocarbons because of the stability of their single covalent bonds. One reaction alkanes do undergo is combustion. Because alkanes make up a large proportion of gaseous and liquid fossil fuels, combustion is their most important reaction. Complete combustion of hydrocarbons produces energy, CO_2, and H_2O. The reaction for the combustion of methane produces 890 kJ/mol.

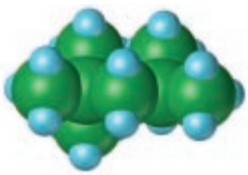
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

One concern about the combustion of fossil fuels is their possible contribution to the greenhouse effect. CO_2 is one of the atmospheric molecules that absorbs infrared radiation. Increased levels of CO_2 through the combustion of fossil fuels may increase the amount of infrared energy absorbed by the atmosphere to a level that can increase the average temperature of Earth.

Engines can be powered by gasoline combustion. When fuel ignites spontaneously before it is reached by the flame front, there is a decrease in the amount of power gained, and engine knocking results. Straight-chain hydrocarbons are more likely to ignite spontaneously than branched-chain hydrocarbons. This tendency is the basis for the octane rating scale. *The* **octane rating** *of a fuel is a measure of its burning efficiency and its antiknock properties*. The octane rating scale is based on mixtures of 2,2,4-trimethylpentane, a highly branched alkane, and heptane, a straight-chain alkane. The term *octane* comes from the common name of 2,2,4-trimethylpentane, *isooctane*. Pure 2,2,4-trimethylpentane is very resistant to knocking and is assigned an octane number of 100. Pure heptane has an octane number of 0 and burns with a lot of knocking. Increasing the percentage of branched-chain alkanes in gasoline is one way to increase octane rating. The octane rating on gasoline pumps is shown in Figure 20-14.



heptane



2,2,4-trimethylpentane

FIGURE 20-14 The octane rating scale is based on a rating of 100 for 2,2,4-trimethylpentane and 0 for heptane. Compare their molecular shapes.

SECTION REVIEW

1. What is the basic structural characteristic of alkanes?
2. Draw all of the condensed structural formulas that can represent C_5H_{12}.
3. Give the systematic name for each of the compounds whose formulas appear in item 2.
4. Relate the properties of some alkanes to their uses.
5. Draw the condensed structural formulas of 3,4-dimethylhexane and 1-methyl-3-propylcyclopentane.

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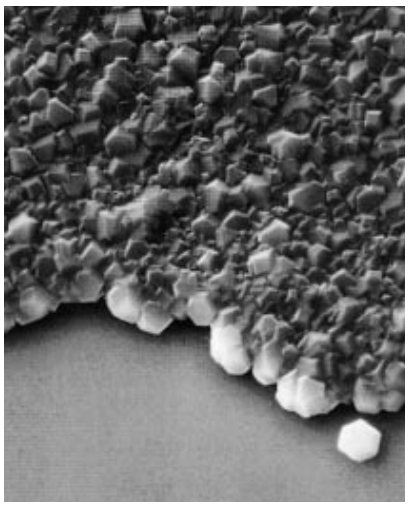
Synthetic Diamonds

Diamonds made to order? Almost. A thin coating of diamond film may not be pretty to look at, but it does offer many useful properties to industry. A number of methods are being developed to produce diamond coatings cheaply and efficiently. If successful, the processes will affect the way tools, containers, computer chips, and a host of other items are manufactured.

James Adair is an associate professor of material science and engineering at the University of Florida. "Natural diamonds are made at very, very high pressures and heat," Adair says. "Basically, it's a naturally occurring process that literally took millennia to form the diamond. We make diamonds in a couple of minutes." The process involves sticking very fine diamond particles on all kinds of different surfaces. Chemical Vapor Deposition is then used to grow more diamond from these diamond "seeds."

In Chemical Vapor Deposition, the objects to be coated—in this case, the diamond seeds—are placed inside a chamber filled with methane and other gases. The gases are subjected to microwave radiation, which breaks them down into hydrogen, carbon, and its mixtures (carbon-hydrogen radicals). Diamond crystals grow when these carbon atoms coat the diamond-seed crystals.

Another method of coating with diamond, invented by metallurgist Pravin Mistry, uses lasers to scan the object to be coated. The energy of the lasers breaks down CO_2 (supplied by a gas delivery system) into carbon and oxygen atoms and vaporizes the surface of the object, forming a superheated plasma. The plasma serves as an environment for bonding the carbon atoms into a coating of crystalline diamond.



This picture, taken with an electron microscope, shows synthetic diamond formed by Chemical Vapor Deposition.

One of the biggest challenges in making synthetic diamond coatings is making sure that the carbon crystallizes correctly to form diamond and not graphite. Graphite is useful for making lubricants and pencil leads, but it is not as strong and durable as diamond. In the crystalline molecular structure of graphite, the spaces between carbon atoms are relatively far apart. The process must compress the spaces to form a compact octagonal diamond crystal.

Diamond is one of the hardest materials known to man, so diamond coatings would be particularly useful for making machine tools, work surfaces, and other applications where a durable protective covering is needed. Diamond also has the highest thermoconductivity of any material, which means that it transports heat very effectively. You wouldn't want to drink from a diamond coffee cup because the cup would warm up rapidly and you'd burn your lips. But diamond's ability to conduct heat makes it very useful as a coating on silicon computer chips.

"For microelectronics," says Adair, "dealing with the heat generated by the circuit is one of the biggest problems. If the heat builds up too much within a silicon circuit, it can literally melt the silicon. And it's not going to act as a very good computer brain for you. Diamond can pull that heat out of the silicon chip, so the circuit can run a little bit cooler."

If a computer chip is prevented from getting too hot, it can perform faster. And a faster chip can lead to a new breed of computers with enhanced capabilities.

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Unsaturated Hydrocarbons

SECTION 20-4

Objectives

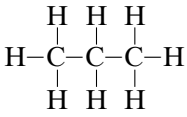
- Distinguish between the structures of alkenes, alkynes, and aromatic hydrocarbons.
- Be able to name and write structural formulas for unsaturated hydrocarbons.
- Explain how structures of unsaturated hydrocarbons relate to their properties and how those properties affect the uses of specific hydrocarbons.

Hydrocarbons that do not contain the maximum amount of hydrogen are referred to as unsaturated. **Unsaturated hydrocarbons** *are hydrocarbons in which not all carbon atoms have four single covalent bonds.*

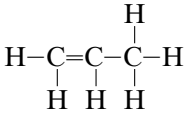
Alkenes

Alkenes *are hydrocarbons that contain double covalent bonds.* Some examples of alkenes are given in Table 20-7. Notice that because alkenes have a double bond, the simplest alkene, ethene, has two carbon atoms.

Carbon atoms linked by double bonds cannot bind as many atoms as those that are linked by only single bonds. An alkene with one double bond has two fewer hydrogen atoms than the corresponding alkane.



C_3H_8



C_3H_6

Thus, the general formula for noncyclic alkenes with one double bond is C_nH_{2n}.

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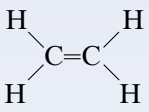
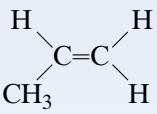
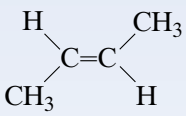
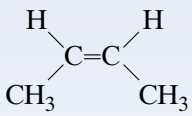
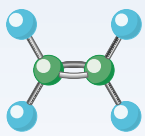
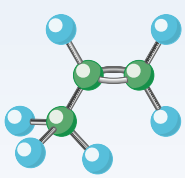
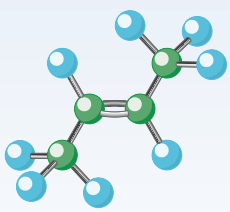
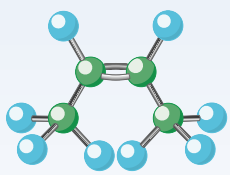
***sci*LINKS CODE:** HC2205

TABLE 20-7 *Structures of Alkenes*

	ethene	propene	*trans*-2-butene	*cis*-2-butene
Structural formula				
Ball-and-stick model				

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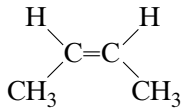
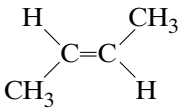
Because alkenes have a double bond, they can have geometric isomers, as shown in the examples below.



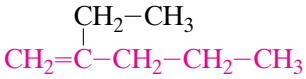
cis-2-butene



trans-2-butene

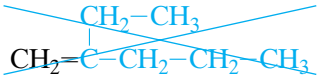
Systematic Names of Alkenes

The rules for naming a simple alkene are similar to those for naming an alkane. The parent hydrocarbon is the longest continuous chain of carbon atoms *that contains the double bond*. If there is only one double bond, the suffix *-ene* is added to the carbon-chain prefix. Here, the longest chain that contains the double bond has five carbon atoms and one double bond, so the parent hydrocarbon is pentene.



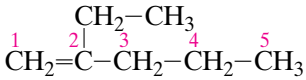
pentene

NOT



~~hexane~~

The carbon atoms in the chain are numbered so that the first carbon atom in the double bond has the lowest number. The number indicating the position of the double bond is placed before the name of the hydrocarbon chain and separated by a hyphen.



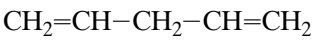
1-pentene

The position number and name of the alkyl group are placed in front of the double-bond position number. This alkyl group has two carbon atoms, an ethyl group. It is on the second carbon atom of the parent hydrocarbon.

2-ethyl-1-pentene

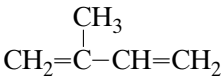
The molecule is 2-ethyl-1-pentene.

If there is more than one double bond, the suffix is modified to indicate the number of double bonds: 2 = *-adiene*, 3 = *-atriene*, and so on.



1,4-pentadiene

If numbering from both ends gives equivalent positions for the double bonds in an alkene with two double bonds, then the chain is numbered from the end nearest the first alkyl group.



2-methyl-1,3-butadiene

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The procedure for naming alkenes can be summarized as follows.

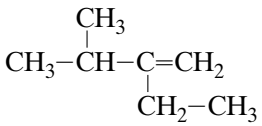
Alkene Nomenclature

Use the rules for alkane nomenclature on page 639, with the following exceptions.

1. **Name the parent hydrocarbon.** Locate the longest continuous chain that *contains the double bond(s)*. If there is only one double bond, add the suffix *-ene* to the prefix corresponding to the number of carbon atoms in this chain. If there is more than one double bond, modify the suffix to indicate the number of double bonds. For example, 2 = *-adiene,* 3 = *-atriene,* and so on.
2. **Add the names of the alkyl groups.**
3. **Number the carbon atoms in the parent hydrocarbon.** Number the carbon atoms in the chain so that the first carbon atom in the double bond nearest the end of the chain has the lowest number. If numbering from both ends gives equivalent positions for two double bonds, then number from the end nearest the first alkyl group.
4. **Insert position numbers.** Place double-bond position numbers immediately before the name of the parent hydrocarbon alkene. Place alkyl group position numbers immediately before the name of the corresponding alkyl group.
5. **Punctuate the name.**

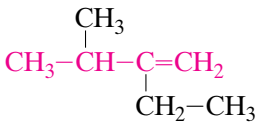
SAMPLE PROBLEM 20-3

Name the following alkene.



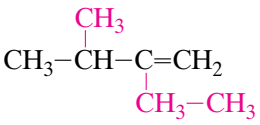
SOLUTION

1. Identify and name the parent hydrocarbon.



The parent hydrocarbon has four carbon atoms and one double bond, so it is named *butene*.

2. Identify and name the alkyl groups.



The alkyl groups are *ethyl* and *methyl*.
Place their names in front of the name of the parent hydrocarbon in alphabetical order.

ethyl methyl butene

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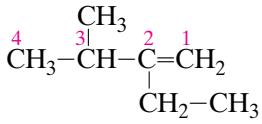
3. Number the carbon chain to give the double bond the lowest position.



4. Place the position number of the double bond in front of butene. Place the position numbers of the alkyl groups in front of each alkyl group. Separate the numbers from the name with hyphens.

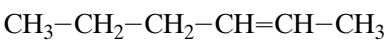
The first carbon in the double bond is in position *1*.
The ethyl group is on carbon *2*.
The methyl group is on carbon *3*.

2-ethyl-**3**-methyl-**1**-butene

The full name is 2-ethyl-3-methyl-1-butene.

PRACTICE

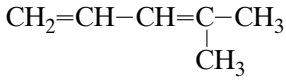
1. Name the following alkene:



Answer
2-hexene

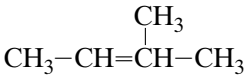
2. Draw the condensed structural formula for 4-methyl-1,3-pentadiene.

Answer



3. Name the following alkenes:

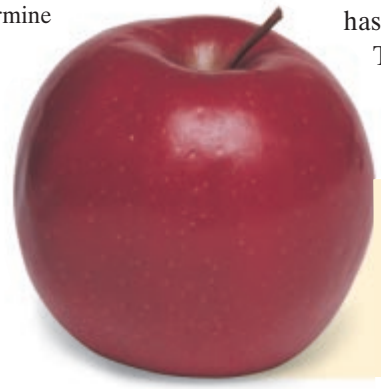
a.



b.

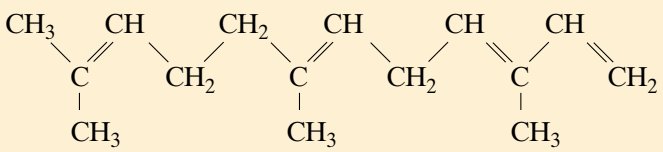
Answer
a. 2-methyl-2-butene
b. 2-methyl-3-hexene

FIGURE 20-15 α-farnesene is a solid alkene found in the natural wax covering of apples. Can you determine the IUPAC name for this large alkene?



Properties and Uses of Alkenes

Alkenes are nonpolar and show trends in properties similar to those of alkanes in boiling points and physical states. For example, α-farnesene has 15 carbon atoms and 4 double bonds, as shown in Figure 20-15. This large alkene is a solid at room temperature and atmospheric pressure. It is found in the natural wax covering of apples. Ethene, the smallest alkene, is a gas.



α-farnesene

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Ethene is the hydrocarbon commercially produced in the greatest quantity in the United States. It is used in the synthesis of many plastics and commercially important alcohols. Ethene is also an important plant hormone. Induction of flowering and fruit ripening, as shown in Figure 20-16, are effects of ethene hormone action that can be manipulated by commercial growers.

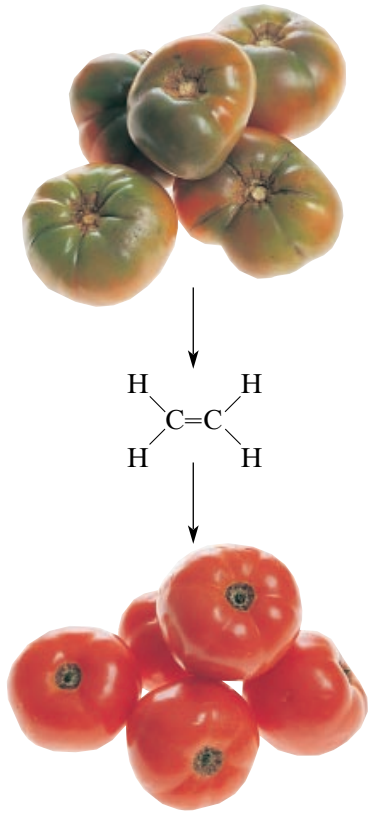


FIGURE 20-16 Ethene is a plant hormone that triggers fruit ripening. Its small size allows it to travel as a gas.

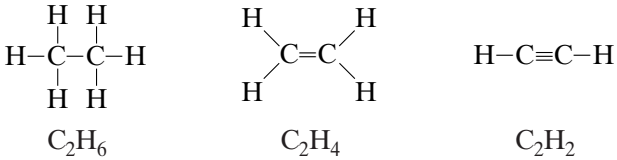
Alkynes

Hydrocarbons with triple covalent bonds are **alkynes.** Like the double bond of alkenes, the triple bond of alkynes requires that the simplest alkyne has two carbon atoms.

$$H{-}C{\equiv}C{-}H$$

ethyne

The general formula for the alkynes is C_nH_{2n-2}. Alkynes have four fewer hydrogen atoms than the corresponding alkanes and two fewer than the corresponding alkenes.



C_2H_6 C_2H_4 C_2H_2

Systematic Naming of Alkynes

Alkyne nomenclature is almost the same as alkene nomenclature. The only difference is that the *-ene* suffix of the corresponding alkene is replaced with *-yne*. A complete list of rules follows.

Alkyne nomenclature

Use the rules for alkane nomenclature on page 639, with the following exceptions.

1. **Name the parent hydrocarbon.** Locate the longest continuous chain that *contains the triple bond(s)*. If there is only one triple bond, add the suffix *-yne* to the prefix corresponding to the number of carbon atoms in the chain. If there is more than one triple bond, modify the suffix to indicate the number of triple bonds. For example, 2 = *-adiyne,* 3 = *-atriyne,* and so on.
2. **Add the names of the alkyl groups.**
3. **Number the carbon atoms in the parent hydrocarbon.** Number the carbon atoms in the chain so that the first carbon atom in the triple bond nearest the end of the chain has the lowest number. If numbering from both ends gives the same positions for two triple bonds, then number from the end nearest the first alkyl group.

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FIGURE 20-17 Ethyne is the fuel used in oxyacetylene torches. Oxyacetylene torches can reach temperatures of over 3000°C.

4. **Insert position numbers.** Place the position numbers of the triple bonds immediately before the name of the parent hydrocarbon alkyne. Place alkyl group position numbers immediately before the name of the corresponding alkyl group.
5. **Punctuate the name.**

Two examples of correctly named alkynes are given below.

$CH_3-CH_2-CH_2-C\equiv CH$

1-pentyne

$CH\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

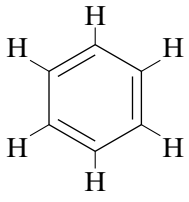
3-methyl-1-butyne

Properties and Uses of Alkynes

Alkynes are nonpolar and exhibit the same trends in boiling points and physical state as other hydrocarbons. The smallest alkyne, ethyne, is a gas. The combustion of ethyne when it is mixed with pure oxygen produces the intense heat of welding torches, as shown in Figure 20-17. The common name of ethyne is *acetylene,* and these welding torches are commonly called oxyacetylene torches.

Aromatic Hydrocarbons

Aromatic hydrocarbons *are hydrocarbons with six-membered carbon rings and delocalized electrons.* **Benzene** *is the primary aromatic hydrocarbon.* The molecular formula of benzene is C_6H_6. One possible structural formula is a six-carbon atom ring with three double bonds.



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However, benzene does not behave chemically like an alkene. All of the carbon–carbon bonds in the molecule are the same. Like graphite, benzene contains resonance hybrid bonds. The structure of the benzene ring allows the delocalized electrons to be spread over the ring. The entire molecule lies in the same plane, as shown in Figure 20-18. The following structural formulas are often used to show this spreading of electrons. In the condensed form, the hydrogen atom at each corner is understood.

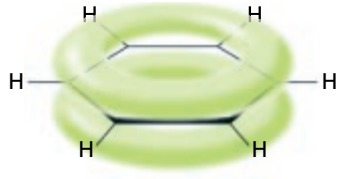
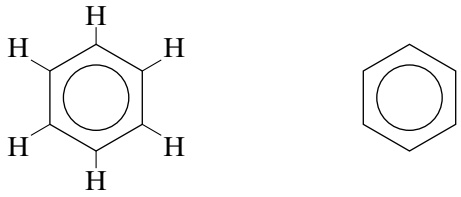
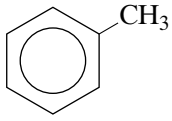


FIGURE 20-18 Electron orbitals in benzene overlap to form continuous orbitals that allow the delocalized electrons to spread uniformly over the entire ring.



Aromatic hydrocarbons can be thought of as derivatives of benzene. The simplest have one benzene ring, as shown in the following example.



methylbenzene

Systematic Names of Aromatic Hydrocarbons

The simplest aromatic hydrocarbons are named as alkyl-substituted benzenes. The names of the alkyl groups are added in front of the word *benzene* according to the rules for other hydrocarbons. As with cycloalkanes, the carbon atoms in the ring do not need to be numbered if there is only one alkyl group. If there is more than one alkyl group, the carbons are numbered in order to give all of the alkyl groups the lowest possible numbers. Following are some examples.

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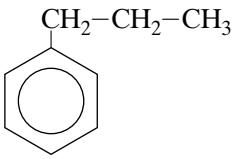
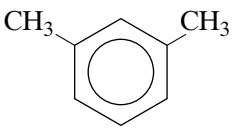


propylbenzene



1,3-dimethylbenzene

The rules for naming simple aromatic hydrocarbons can be summarized as follows.

Simple Aromatic Hydrocarbon Nomenclature

Use the rules for alkane nomenclature on page 639, with the following exceptions.

1. **Name the parent hydrocarbon.** The parent hydrocarbon is the benzene ring, *benzene*.
2. **Add the names of the alkyl groups.**

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3. **Number the carbon atoms in the parent hydrocarbon.** If there are two or more alkyl groups attached to the benzene ring, number the carbon atoms in the ring. Assign position number one to the alkyl group that comes first in alphabetical order. Then number in the direction that gives the rest of the alkyl groups the lowest numbers possible.
4. **Insert position numbers.**
5. **Punctuate the name.**

SAMPLE PROBLEM 20-4

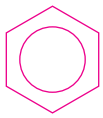
Draw the condensed structural formula for 1,2-dimethylbenzene.

SOLUTION

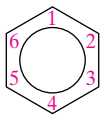
1. Identify the parent hydrocarbon in the name.

1,2-dimethyl**benzene**

2. Draw the benzene ring.



3. Number the carbon atoms in the benzene ring.



4. Identify any alkyl groups.

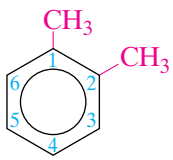
1,2-di**methyl**benzene

There are only methyl groups in this molecule. The prefix *di-* is attached to the word *methyl,* so there are two methyl groups.

5. Locate the position numbers for the methyl groups.

1,2-dimethylbenzene

6. Attach the methyl groups to the carbon atoms numbered *1* and *2*.



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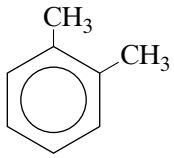
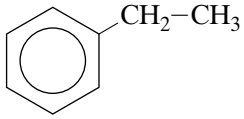
7. The complete structural formula for 1,2-dimethylbenzene is as follows.



PRACTICE

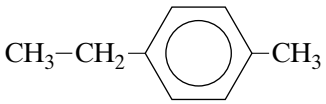
1. Name the following compound:



Answer
ethylbenzene

2. Draw the condensed structural formula for 1-ethyl-4-methylbenzene.

Answer



Properties and Uses of Aromatic Hydrocarbons

Benzene rings are chemically very stable, a property that can be explained by the concept of delocalized electrons. Therefore, aromatic hydrocarbons are less reactive than alkenes and alkynes are. In the past, benzene was used as a nonpolar solvent because of this stability. However, benzene is both a poison and a carcinogen. Like other hydrocarbons, benzene is nonpolar and has limited solubility in water. It appears that oxidation of the benzene ring, in an attempt to solubilize it for elimination from the body, produces toxic molecules. This has led to the replacement of benzene as a solvent with methylbenzene, which is less toxic. Another aromatic hydrocarbon, 3,4-benzpyrene, is found in coal tar, tar from cigarette smoke, and soot in heavily polluted urban areas. Studies have shown this compound can cause cancer.

SECTION REVIEW

1. List the basic structural features that characterize each of the following:
   a. alkenes
   b. alkynes
   c. aromatic hydrocarbons
2. Draw three condensed structural formulas that can represent C_4H_8.
3. Give the systematic name for each compound in your answer to item 2.
4. Give examples of a property or use of three unsaturated hydrocarbons.
5. Draw the condensed structural formula for each of the following:
   a. 1,3-butadiene
   b. 2-pentyne
   c. 1,2-diethylbenzene

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CHAPTER 20 REVIEW

CHAPTER SUMMARY

20-1

- Carbon is important because all living matter contains carbon.
- Hybridized orbitals allow carbon atoms to form single, double, and triple covalent bonds.
- Carbon occurs in several solid allotropic forms, such as diamond, graphite, and fullerenes, all of which have different structures and properties.

Vocabulary

delocalized electrons (627) diamond (626) fullerenes (626) graphite (626)

20-2

- All organic compounds contain carbon, but not all carbon-containing compounds are classified as organic.
- The number of possible organic compounds is virtually unlimited because of the bonding properties of carbon. The unique catenation ability of carbon allows it to link together to form long chains and rings. The ability of carbon to bind other elements and to allow different arrangements of atoms adds to the diversity of carbon compounds.
- Isomers are compounds with the same molecular formula but different structures. Structural formulas are needed to show the bonding order and arrangement of atoms in an organic molecule to distinguish between isomers.
- Structural isomers are isomers in which the atoms are bonded together in different orders. Geometric isomers are isomers in which the order of atom bonding is the same but the atoms are arranged differently in space.

Vocabulary

catenation (630) hydrocarbons (630) organic compounds (629) structural isomers (631)
geometric isomers (632) isomers (630) structural formula (630)

20-3

- In saturated hydrocarbons, each carbon atom has four single covalent bonds. Alkanes are saturated hydrocarbons.
- Organic compounds are named according to a systematic method developed by IUPAC.
- Alkanes contain only single bonds. Because alkanes consist of saturated single covalent bonds, these compounds are not very reactive. One important reaction they do undergo is combustion.
- Trends in physical states, boiling points, and combustion properties correspond to trends in alkane size and amount of branching.

Vocabulary

alkanes (634) fractional distillation (644) natural gas (643) petroleum (643)
alkyl groups (637) homologous series (634) octane rating (645) saturated hydrocarbons (634)
cycloalkanes (635)

20-4

- Carbon atoms in unsaturated hydrocarbons do not all have four single covalent bonds. Alkenes, alkynes, and aromatic hydrocarbons are unsaturated hydrocarbons.
- Alkenes contain carbon-carbon double bonds and can have geometric isomers. The smallest alkene, ethene, is an important industrial and agricultural chemical.
- Alkynes contain carbon-carbon triple bonds.
- Benzene and derivatives of benzene are aromatic hydrocarbons. The concept of delocalized electrons helps explain the stability of the benzene ring.

Vocabulary

alkenes (647) aromatic hydrocarbons (652) benzene (652) unsaturated hydrocarbons (647)
alkynes (651)

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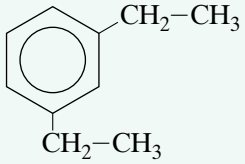
REVIEWING CONCEPTS

1. What is the orientation of the four covalent bonds and the sp^3 orbitals of a carbon atom? (20-1)
2. Name and describe the structures of three allotropic forms of carbon. (20-1)
3. What properties of diamond determine most of its industrial uses? (20-1)
4. Why does graphite conduct electricity while diamond does not? (20-1)
5. Explain why the structure of graphite makes it useful as a lubricant. (20-1)
6. Describe the structure of buckminsterfullerene. (20-1)
7. a. What is catenation?
   b. How does catenation contribute to the diversity of organic compounds? (20-2)
8. What are hydrocarbons, and what is their importance? (20-2)
9. a. What information about a compound is provided by a structural formula?
   b. How are structural formulas used in organic chemistry? (20-2)
10. Can molecules with the molecular formulas C_4H_{10} and $C_4H_{10}O$ be structural isomers of one another? Why or why not? (20-2)
11. Can molecules with only single bonds (and no rings) have geometric isomers? Why or why not? (20-2)
12. a. What do the terms *saturated* and *unsaturated* mean when applied to hydrocarbons?
    b. What other meanings do these terms have in chemistry?
    c. Classify alkenes, alkanes, alkynes, and aromatic hydrocarbons as either saturated or unsaturated. (20-3 and 20-4)
13. Classify each of the following as an alkane, alkene, alkyne, or aromatic hydrocarbon.

    a. 

    b. $CH_3-CH=CH_2$

    c. $CH\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

    d. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_2-CH_3$

    (20-3 and 20-4)
14. Give the general formula for the members of the following:
    a. alkane series
    b. alkene series
    c. alkyne series (20-3 and 20-4)
15. Give the molecular formula for each type of hydrocarbon if it contains seven carbon atoms.
    a. an alkane
    b. an alkene
    c. an alkyne (20-3 and 20-4)
16. a. What is a homologous series?
    b. By what method are straight-chain hydrocarbons named?
    c. Name the straight-chain alkane with the molecular formula $C_{10}H_{22}$. (20-3)
17. What are cycloalkanes? (20-3)
18. a. What trend occurs in the boiling points of alkanes?
    b. How would you explain this trend?
    c. How is the trend in alkane boiling points used in petroleum fractional distillation? (20-3)
19. How does the structure of alkanes affect the octane rating of gasoline? (20-3)
20. Write a balanced equation for the complete combustion of each of the following:
    a. methane
    b. ethyne (20-3 and 20-4)
21. Which types of isomers are possible for alkanes (with no rings), alkenes, and alkynes? Why? (20-3 and 20-4)
22. Give examples of ethene's commercial uses. (20-4)
23. a. Alkyne nomenclature is very similar to the nomenclature of what other group of hydrocarbons?
    b. How do these nomenclatures differ? (20-4)

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24. Give one use for ethyne. (20-4)

25. a. What are delocalized electrons?
b. What is their effect on the reactivity of aromatic hydrocarbons? (20-4)

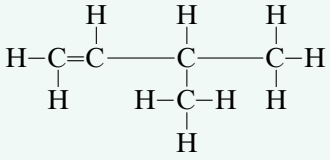
26. What is the name of the parent hydrocarbon of simple aromatic hydrocarbons? (20-4)

27. Describe a possible cause of benzene toxicity. (20-4)

PROBLEMS

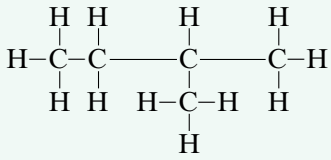
Structural Formulas

28. Draw the condensed structural formula for the following:



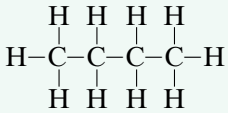
29. Identify each of the following pairs of formulas as representing the same or different molecules:

a. C_5H_{12} AND



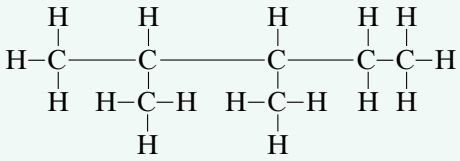
b. $CH_3-CH_2-CH_3$

AND

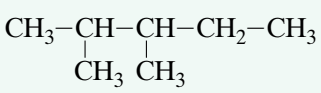


c. C_6H_{10} AND $CH_3-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle \quad}{\underset{|}{C}}}-CH_3$

d.



AND

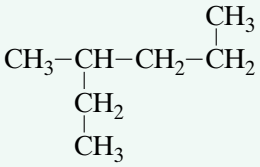


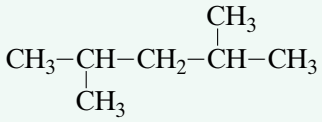
Isomers

30. Identify whether each pair represents the same molecule or structural isomers.

a. $CH_3-CH_2-CH_2-CH_3$ $\qquad$ $\begin{matrix} CH_3 \\ | \\ CH_2-CH_2-CH_3 \end{matrix}$

b.





c.

31. Draw structural formulas for the five isomers of C_6H_{14}.

32. Draw the geometric isomers of the following molecule. Label each isomer as *cis* or *trans*.

$CH_3-CH=CH-CH_2-CH_3$

33. a. Which of the following can have geometric isomers?

$CH_3-CH=CH-Cl$ $\qquad$ $CH_3-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle \quad}{\underset{|}{C}}}-CH_3$

$CH_3-CH_2-CH=CH-CH_2-CH_3$

b. Draw the geometric isomers for those that can have geometric isomers.
c. Label each geometric isomer as *cis* or *trans*.

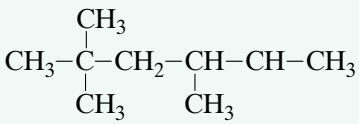
Alkane Nomenclature

34. Name the following molecules. (Hint: See Sample Problem 20-1.)

a. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

b.

c.



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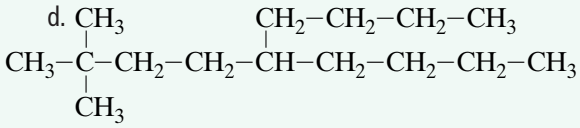
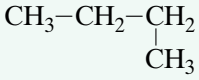
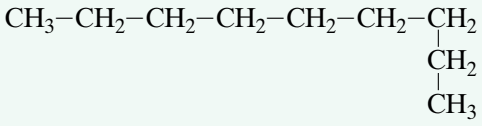
d. 

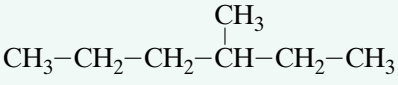
35. Give the complete, uncondensed, structural formula for each of the following alkanes. (Hint: See Sample Problem 20-2.)
a. decane
b. 3,3-dimethylpentane

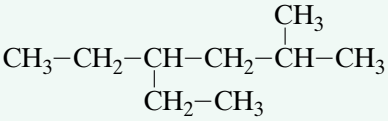
36. Give the condensed structural formula for each of the following alkanes:
a. 1,1-dimethylcyclopropane
b. 2,2,4,4-tetramethylpentane

37. For each of the following, determine whether the alkane is named correctly. If it is not, give the correct name.

a. 
1-methylpropane

b. 
nonane

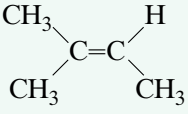
c. 
4-methylhexane

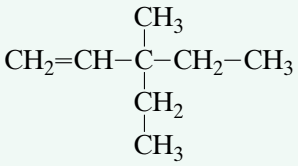
d. 
4-ethyl-2-methylhexane

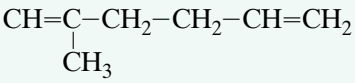
Alkene Nomenclature

38. Name the following alkenes. (Hint: See Sample Problem 20-3.)

a. $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$

b. 

c. 

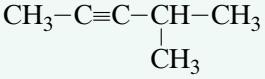
d. 

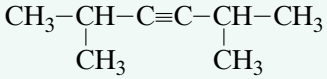
39. Draw the condensed structural formula for each of the following alkenes:
a. 2-methyl-2-hexene
b. 3-ethyl-2,2-dimethyl-3-heptene

40. Draw structural formulas for geometric isomers of each of the following:
a. $CH_3{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3$
b. 3-methyl-2-pentene

Alkyne Nomenclature

41. Name the following alkynes:
a. $CH{\equiv}C{-}CH_3$

b. 

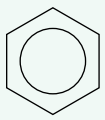
c. 

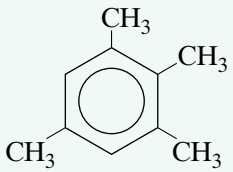
d. $CH{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}C{\equiv}CH$

42. Draw the condensed structural formula for each of the following alkynes:
a. 1-decyne
b. 6,6-dimethyl-3-heptyne

Aromatic Hydrocarbon Nomenclature

43. Name the following aromatic hydrocarbons. (Hint: See Sample Problem 20-4.)

a. 

b. 

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44. Draw the condensed structural formula for each of the following molecules:
a. 1,3,5-trimethylbenzene
b. 1,3-dimethylbenzene

Calculations with Carbon Compounds

45. The jewelers' mass unit for diamond is the carat. By definition, 1 carat equals exactly 200 mg. What is the volume of a 1.00 carat diamond? The density of diamond is 3.51 g/cm^3.

46. For 100.0 g of butadiene, C_4H_6, calculate the following:
a. number of moles
b. number of molecules

47. An alkene has the molecular formula $C_{12}H_{24}$. Determine its percent composition.

48. Assuming that the volumes of carbon dioxide and of propane are measured under the same experimental conditions, what volume of carbon dioxide is produced by the complete combustion of 15.0 L of propane?

49. Assume a gasoline is isooctane, which has a density of 0.692 g/mL. What is the mass in kilograms of 12.0 gal of the gasoline (1 gal = 3.78 L)?

MIXED REVIEW

50. a. Draw the complete, uncondensed structural formula for 4-methyloctane.
b. Convert it into the condensed structural formula.
c. Determine the molecular formula for the molecule from both the structure you drew and the general molecular formula for alkanes. Compare the two. Are they the same?

51. Draw and name two different condensed structural formulas for molecules of each of the following types of hydrocarbons containing eight carbon atoms:
a. alkane
b. alkene
c. alkyne
d. aromatic hydrocarbon

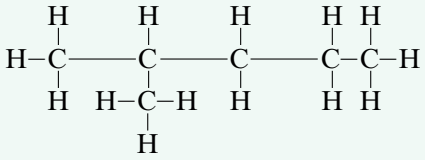
52. Draw the condensed structural formulas for 4,4-dimethyl-2-pentyne and 2,2-dimethyl-4-propyloctane.

53. Draw the three structural isomers for an alkyne containing five carbon atoms and one triple bond. Name the molecules you draw.

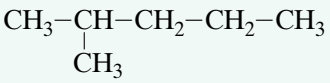
54. Which of the following molecules have geometric isomers? Draw all possible geometric isomers. Label the molecules you draw as either *cis* or *trans*.
a. butane
b. 2-pentene
c. 2-hexyne
d. 2-methyl-1-butene

55. Identify the following pairs as the same compound, isomers, or different compounds that are not isomers:

a.

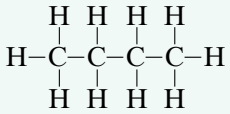


AND

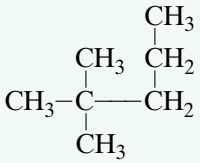


b. C_4H_8

AND



c.



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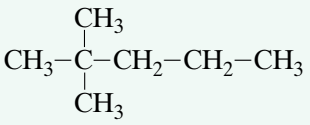
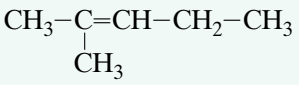
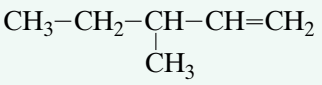


d. 

AND



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CRITICAL THINKING

56. Inferring Conclusions Why are organic compounds with covalent bonds usually less stable when heated than inorganic compounds with ionic bonds?

57. Inferring Relationships The element that appears in the greatest number of compounds is hydrogen. The element found in the second greatest number of compounds is carbon. Why are there more hydrogen compounds than carbon compounds?

58. Relating Ideas As the number of carbon atoms in an alkane molecule increases, does the percentage of hydrogen increase, decrease, or remain the same?

HANDBOOK SEARCH

59. The top 10 chemicals produced in the United States are listed in Table 7B of the *Elements Handbook.* Review this material, and answer the following:
- a. Which of the top ten compounds are organic?
- b. Write structural formulas for the compounds you listed in item (a).
- c. To what homologous series do each of these compounds belong?

60. The reaction of methane with oxygen produces two different oxides of carbon. Review this material in the *Elements Handbook,* and answer the following:
- a. What conditions determine whether the product of the methane reaction is CO_2 or CO?
- b. If a home heating system is fueled by natural gas, what difference does it make if the combustion produces CO_2 or CO?

61. Silicon is similar to carbon in forming long-chain compounds. Review the material on silicon in the *Elements Handbook* and answer the following.
- a. How does a long-chain silicon compound differ in composition from a long-chain carbon compound?
- b. The simplest alkane is methane. Methyl groups are found in all alkanes. What is a common subunit of a silicate? What is the geometry of that subunit?

62. Mercury in the environment poses a hazard to living things. Review the section on mercury poisoning in the *Elements Handbook.*
- a. Draw a structure formula for the organic mercury compound described in that section.
- b. What is the IUPAC name for this compound?

RESEARCH & WRITING

63. *Chemical and Engineering News* publishes a list once a year of the top 50 chemicals. Find out which chemicals on the current year's list are hydrocarbons, and report your findings to the class.

64. Consult reference materials at the library, and read about products made from hydrocarbons. Keep a list of the number of petroleum-related products you use in a single day.

ALTERNATIVE ASSESSMENT

65. Performance Models are often used to visualize the three-dimensional shape of molecules. Using gumdrops as atoms and toothpicks to bond them together, construct models of different hydrocarbons. Use large gumdrops for carbon and smaller gumdrops for hydrogen. Refer to Figures 20-1 and 20-2 for guidelines on the three-dimensional shapes of hydrocarbons.

66. Performance Using your gumdrop models, demonstrate why alkenes can have geometric isomers, while alkanes cannot.

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CHAPTER 21

Other Organic Compounds

Organic compounds are used to make many of the products we use every day.

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Functional Groups and Classes of Organic Compounds

SECTION 21-1

Objectives

- Define *functional group,* and explain why functional groups are important.
- Identify alcohols, alkyl halides, and ethers based on the functional group present in each.
- Classify alcohols, alkyl halides, and ethers from names and structural formulas.
- Relate properties of alcohols, alkyl halides, and ethers to their structures. Describe how these properties influence the uses of specific organic compounds.

A **functional group** *is an atom or group of atoms that is responsible for the specific properties of an organic compound;* the bonds within functional groups are often the site of chemical reactivity. A given functional group undergoes the same types of chemical reactions in every molecule in which it is found. Therefore, all compounds that contain the same functional group have similar properties and can be classified together.

Alcohols

Alcohols *are organic compounds that contain one or more hydroxyl groups.* The general formula for a class of organic compounds consists of the functional group and the letter *R,* which stands for the rest of the molecule. The general formula for alcohols is $R{-}OH$. Systematic names of organic compounds indicate which functional groups are present in a molecule. The rules for naming simple alcohols are as follows.

Alcohol Nomenclature

1. **Name the parent compound.** Locate the longest continuous chain of carbon atoms *that contains the hydroxyl group*. If there is only one hydroxyl group, change the final *-e* in the name of the corresponding alkane to *-ol*. If there is more than one hydroxyl group, use the full name of the corresponding alkane and add the suffix modified to indicate the number of hydroxyl groups. For example, *-diol* = 2, *-triol* = 3, and so on.
2. **Number the carbon atoms in the parent chain.** Number the carbon atoms in the chain so that the hydroxyl groups have the lowest numbers possible.
3. **Insert position numbers.** Place the hydroxyl position number or numbers immediately before the name of the parent alcohol.
4. **Punctuate the name.** Separate the position numbers from the name with a hyphen. If there is more than one position number, separate the position numbers with commas.

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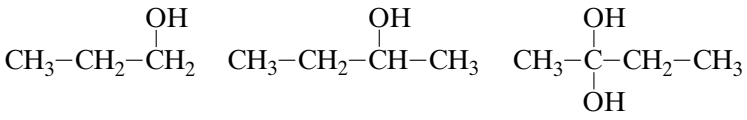
TABLE 21-1 Boiling Points of Some Alcohols and Alkanes

Compound	Molecular formula	Molar mass (g/mol)	Boiling point (°C)
methanol	CH_3OH	32	64.7
ethane	C_2H_6	30	–88
ethanol	C_2H_5OH	46	78.3
propane	C_3H_8	44	–42.1
1-propanol	C_3H_7OH	60	97.2
butane	C_4H_{10}	58	–0.50

Following are three examples of correctly named alcohols.



1-propanol 2-butanol 2,2-butanediol

Properties and Uses of Alcohols

As shown in Table 21-1, the boiling points of alcohols tend to be higher than those of alkanes of comparable molar mass. For example, the molar mass of ethanol, 46 g/mol, is close to that of propane, 44 g/mol. However, their boiling points are very different. The boiling point of ethanol is 78.3°C, while the boiling point of propane is –42.1°C. In addition, boiling points increase as the number of hydroxyl groups in the molecule increases. This trend can be seen in Table 21-2, which shows the boiling points for alcohols with one, two, and three hydroxyl groups.

The boiling point trends shown in Tables 21-1 and 21-2 can be explained by hydrogen bonding, which was discussed in Chapter 6. Compared to alkanes, extra energy is required to break hydrogen bonds between alcohol molecules before conversion from a liquid to a gas. When more than one hydroxyl group is present, an alcohol molecule may form multiple hydrogen bonds. In this case, even more energy is required to break the hydrogen bonds before the liquid is converted to a gas.

TABLE 21-2 Multiple Hydroxyl Groups and Boiling Points

Alcohol	Number of hydroxyl groups	Boiling point (°C)
ethanol	1	78.3
1,2-ethanediol	2	197.3
1-propanol	1	97.2
1,2-propanediol	2	188
1,2,3-propanetriol	3	258–260

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TABLE 21-3 Solubility of Some Alcohols in Water

Alcohol	Molecular formula	Solubility (g/100. g of water)
methanol	CH_3OH	∞ (completely soluble)
1-butanol	C_4H_9OH	7.4
1-pentanol	$C_5H_{11}OH$	2.7
1-octanol	$C_8H_{17}OH$	0.06

As explained in Chapter 13, alcohols are soluble in water because of hydrogen bonding. However, the solubility of alcohols in water tends to decrease with an increase in the size of the molecule. The longer the hydrocarbon chain in an alcohol, the larger the nonpolar, insoluble portion of the molecule. Table 21-3 illustrates this trend.

Hydrogen bonding in alcohols can also explain other properties and uses of alcohols. Cold creams, lipsticks, body lotions, and similar products generally include 1,2,3-propanetriol, commonly called glycerol, to keep them moist. A model for glycerol is shown in Figure 21-1. Multiple hydroxyl groups allow glycerol to form many hydrogen bonds with water molecules in the air or in the surrounding material.

Alcohols are sometimes used today as alternative fuels and as octane enhancers in fuel for automobiles. Ethanol is combined with gasoline, for example, in a one-to-nine ratio to produce gasohol. Some experts have promoted the use of gasohol as a fuel for automobiles because it burns more cleanly, helps save valuable petroleum reserves, and reduces our nation's dependence on foreign imports of petroleum. However, there are also disadvantages. The combustion of ethanol produces only 60% as much energy per gram as does the combustion of gasoline. The presence of ethanol also causes increased water absorption in the fuel.

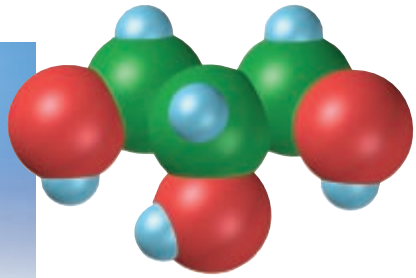

FIGURE 21-1 Glycerol contains three hydroxyl groups. This structure allows it to form multiple hydrogen bonds with water. Glycerol is added as a moisturizer to skin products.

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All simple alcohols are poisonous to some extent. When ethanol is consumed, it is broken down by the enzyme alcohol dehydrogenase. This enzyme rapidly converts ethanol to an oxidized form known as acetaldehyde, which is then converted to acetic acid. Acetic acid, a component of household vinegar, is relatively harmless to the human body. However, consuming large amounts of ethanol can be fatal. The lethal dose varies for different individuals. The amount of ethanol found in a liter of hard liquor, 400 mL, is usually fatal.

Other simple alcohols are attacked by alcohol dehydrogenase more slowly, making these alcohols more toxic than ethanol. For example, methanol, or wood alcohol, is converted to formaldehyde and formic acid, both of which are toxic. A great deal of damage can be done to cells before these chemicals are completely metabolized by the body. Methanol is about 10 times more toxic than is ethanol. Toxic effects of methanol include damage to the optic nerve, coma, and death.

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Alkyl Halides

Alkyl halides *are organic compounds in which one or more halogen atoms—fluorine, chlorine, bromine, or iodine—are substituted for one or more hydrogen atoms in a hydrocarbon.* Because *–X* is often used to represent any halogen, an alkyl halide may be represented by the general formula $R{-}X$. The rules for naming simple alkyl halides in the IUPAC system are as follows.

Alkyl Halide Nomenclature

1. **Name the parent compound.** Locate the longest continuous chain of carbon atoms. Add the prefixes for the attached halogen atoms to the name of the alkane corresponding to the number of carbon atoms in this chain. The prefixes to use are *fluoro-* for fluorine, *chloro-* for chlorine, *bromo-* for bromine, and *iodo-* for iodine. If more than one kind of halogen atom is present, add the halogen prefixes in alphabetical order. If there is more than one atom of the same halogen, add the appropriate prefix (*di-*, *tri-*, and so on) after the prefixes are arranged in alphabetical order.
2. **Number the carbon atoms in the parent chain.** Number the carbon-atom chain so that the lowest number is in the name. If there are different halogen atoms in equivalent positions, give the lower number to the one that comes first in alphabetical order.
3. **Insert position numbers.** Place the halogen position number or numbers immediately before the halogen prefixes.
4. **Punctuate the name.** Separate the position numbers from the name with hyphens. If there is more than one position number, separate the position numbers with commas.

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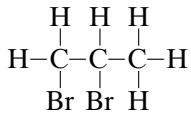
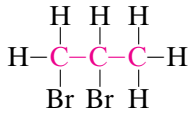
SAMPLE PROBLEM 21-1

Name the alkyl halide shown.



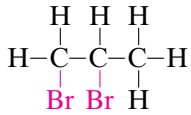
SOLUTION

1. Locate the longest continuous chain of carbon atoms that contains the halogen.



The chain has three carbon atoms, so the name of the chain is *propane.*

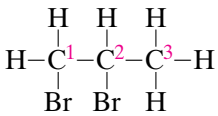
2. Identify and name the halogen atoms attached to the chain.



Bromine atoms are attached to the chain. Add the prefix *bromo-* in front of *propane.* Add the prefix *di-* to show that there are two bromine atoms present.

dibromopropane

3. Number the carbon-atom chain so that the sum of the halogen numbers is as low as possible.



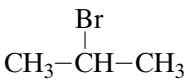
4. The bromine atoms are on carbons numbered *1* and *2.* Place these numbers immediately before the halogen prefix. Separate the numbers from the prefix with a hyphen. Separate the numbers with a comma.

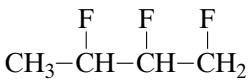
1,2-dibromopropane

The complete name is 1,2-dibromopropane.

PRACTICE

1. Name each of the following alkyl halides:

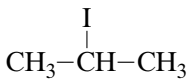
a. 

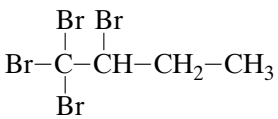
b. 

2. Draw condensed structures for each of the following alkyl halides:
   a. 2-iodopropane
   b. 1,1,1,2-tetrabromobutane

Answer

1. a. 2-bromopropane
   b. 1,2,3-trifluorobutane

2. a. 

   b. 

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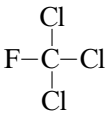
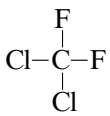
Properties and Uses of Alkyl Halides

Alkyl halides are some of the most widely used organic chemicals. A family of alkyl halides that has received widespread attention in recent years is the chlorofluorocarbons, or CFCs. *CFCs* are alkyl halides that contain both chlorine and fluorine. The formulas for two widely used CFCs, Freon-11 and Freon-12, are shown below.



trichlorofluoromethane
(Freon-11)



dichlorodifluoromethane
(Freon-12)

CFC-11 and CFC-12 are odorless, nontoxic, nonflammable, and very stable. They also easily change physical states. These properties make them useful in a number of commercial operations. They have been used in the manufacture of plastic foam and as liquid refrigerants in commercial refrigerators. At the height of their production, in 1985, more than 700 million kilograms of CFC-11 and CFC-12 were manufactured worldwide.

However, CFCs contribute to the destruction of ozone in the upper atmosphere, as shown in Figure 21-2. When released into the atmosphere, CFCs can break down and release free chlorine atoms.

$$CCl_2F_2 \xrightarrow{\text{solar radiation}} Cl + CClF_2$$

The released chlorine atoms attack molecules of ozone (O_3) found in the upper atmosphere. The ozone is converted to diatomic oxygen.

$$Cl + O_3 \longrightarrow ClO + O_2$$

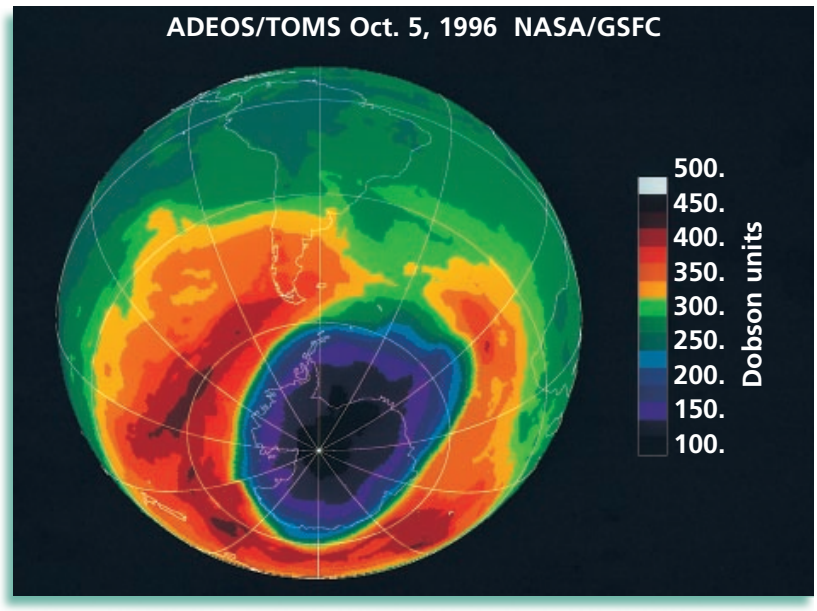


FIGURE 21-2 The depletion of ozone in the upper atmosphere above Antarctica has produced an area of very low ozone concentration, called the ozone hole. The black region over Antarctica shows the area of greatest ozone depletion.

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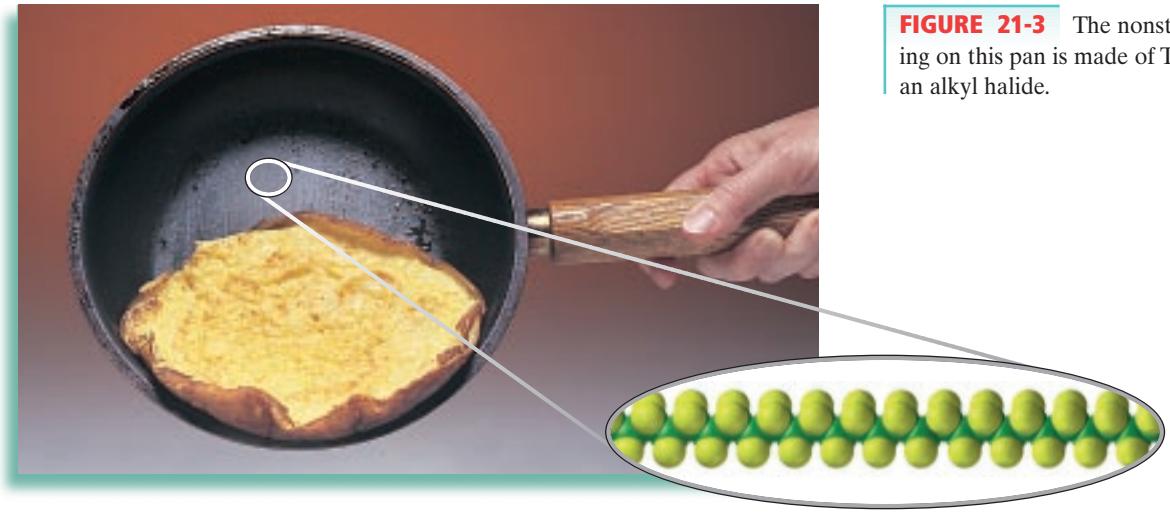

FIGURE 21-3 The nonstick coating on this pan is made of Teflon, an alkyl halide.

Chlorine atoms are eventually regenerated.

$$ClO + O \longrightarrow Cl + O_2$$

This makes it possible for a single chlorine atom to destroy thousands of ozone molecules.

The depletion of ozone in the upper atmosphere has produced an area of very low concentration, called an ozone hole, over Antarctica. Ozone molecules absorb ultraviolet radiation from sunlight, preventing most of that radiation from reaching Earth. Ultraviolet radiation is known to cause skin cancer in humans, to kill some forms of microscopic life, to damage plant tissue, and to cause other harmful effects in plants and animals. Because CFCs are a major cause of ozone depletion, more than 100 nations signed an agreement in 1987 to reduce the amount of CFCs produced.

Another alkyl halide is tetrafluoroethene, C_2F_4. It is joined in long chains to make a material with the trade name Teflon. Because of the unreactive carbon-fluorine bond, Teflon is inactive and stable to about 325°C. It also has a low coefficient of friction, which means that other objects slide smoothly over its surface. These properties enable Teflon to be used in heat-resistant machine parts that cannot be lubricated. It is also used in making utensils with "nonstick" surfaces, such as the frying pan in Figure 21-3.

Ethers

Ethers *are organic compounds in which two hydrocarbon groups are bonded to the same atom of oxygen.* They can be represented by the general formula $R{-}O{-}R'$. In this formula, R' may be the same hydrocarbon group as R or a different one. One set of rules for naming simple ethers are as follows.

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Ether Nomenclature

1. **Name the parent compound.** The word *ether* will come at the end of the name.
2. **Add the names of the alkyl groups.** If there are two different alkyl groups, arrange the names in alphabetical order in front of the word *ether.* If both alkyl groups are the same, the prefix *di-* is added to the name of the alkyl group in front of the word *ether.*
3. **Leave appropriate spaces in the name.** There should be spaces between the names of the alkyl groups and between the alkyl groups and the word *ether.*

SAMPLE PROBLEM 21-2

Name the ether shown below.

$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$$

SOLUTION

1. The word *ether* will come at the end of the name.

ether

2. Identify and name the two alkyl groups joined to the oxygen atom.

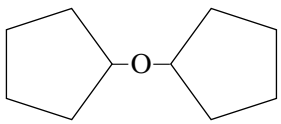
$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$$

They are both ethyl groups. Add the prefix *di-* to show that there are two ethyl groups present. Place *diethyl* in front of *ether,* separated by a space.

diethyl ether

The full name is diethyl ether. Diethyl ether is the most common ether and is also known as ethyl ether, or just ether.

PRACTICE

1. Name each of the following ethers:
   a. $CH_3{-}CH_2{-}CH_2{-}O{-}CH_3$
   b. 
   c. $CH_3{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

Answer

1. a. methyl propyl ether
   b. dicyclopentyl ether
   c. methyl pentyl ether

2. Draw condensed structures for the following ethers:
   a. ethyl propyl ether
   b. dicyclohexyl ether
   c. butyl methyl ether

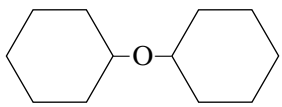
2. a. $CH_3{-}CH_2{-}O{-}CH_2{-}CH_2{-}CH_3$
   b. 
   c. $CH_3{-}CH_2{-}CH_2{-}CH_2{-}O{-}CH_3$

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TABLE 21-4 Comparison of the Boiling Points of an Ether, Alkane, and Alcohol

Compound	Molar mass	Boiling point (°C)
diethyl ether	74	34.6
pentane	72	36.1
1-butanol	74	117.7

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TOPIC: Ethers
GO TO: www.scilinks.org
***sci*LINKS CODE:** HC2213

Properties and Uses of Ethers

The solubilities of ethers and alcohols in water are similar. For example, diethyl ether and 1-butanol have the same molar mass. They also have approximately the same solubility, 6 g/100 g of water for diethyl ether and 7.4 g/100 g of water for 1-butanol. This similarity can be explained by the fact that ethers, like alcohols, can form hydrogen bonds with water molecules.

In comparison, the boiling points of ethers are much lower than those of alcohols of similar molar mass. But, they are about the same as those of alkanes of similar molar mass. This trend is clear from the comparison in Table 21-4. This trend can also be explained by hydrogen bonding. Unlike alcohols, ethers cannot form hydrogen bonds with each other because they do not have a hydrogen atom bonded to a highly electronegative atom. Therefore, no extra energy is needed to break hydrogen bonds for ethers to boil.

Like alkanes, ethers are not very reactive compounds. This property explains their most common uses as solvents. In many organic reactions in which water cannot be used as a solvent, an ether is used instead.

Methyl-*tertiary*-butyl ether (MTBE) is the most widely used ether. It is another gasoline octane enhancer. At one time, tetraethyl lead, $(C_2H_5)_4Pb$, was widely used for this purpose. However, concerns about the release of lead into the environment have increased, so tetraethyl lead has been replaced by MTBE and other octane enhancers.

SECTION REVIEW

1. Give the general formula and class of organic compounds for each of the following:
   a. CH_3-OH
   b. CH_3-O-CH_3
   c. $Br-CH_2-CH_2-CH_3$
2. Give the name of each of the following:
   a. $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$
   b. CH_3-O-CH_3
   c. $CH_3-CH_2-\underset{\displaystyle F}{\underset{|}{\overset{\displaystyle F}{\overset{|}{CH}}}}$
3. Compare the boiling points of alcohols, ethers, and alkanes, and explain one reason for the differences.
4. Draw condensed structures for each of the following:
   a. 1,2-propanediol
   b. ethyl methyl ether
   c. dichloromethane

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SECTION 21-2

More Classes of Organic Compounds

Objectives

- Identify aldehydes, ketones, carboxylic acids, esters, and amines based on the functional group present in each.
- Classify aldehydes, ketones, carboxylic acids, esters, and amines from names and structural formulas.
- Relate properties of aldehydes, ketones, carboxylic acids, esters, and amines to their structures. Describe how these properties influence the uses of specific organic compounds.

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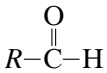
***sci*LINKS CODE:** HC2214

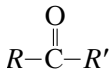
Aldehydes and Ketones

Aldehydes and ketones contain the *carbonyl group*, shown below.

The difference between aldehydes and ketones is the location of the carbonyl group. **Aldehydes** *are organic compounds in which the carbonyl group is attached to a carbon atom at the end of a carbon-atom chain.* **Ketones** *are organic compounds in which the carbonyl group is attached to carbon atoms within the chain.* These differences can be seen in their general formulas, shown below.



aldehyde



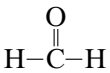
ketone

The IUPAC rules for naming simple aldehydes and ketones are as follows.

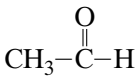
Aldehyde Nomenclature

Name the parent compound. Locate the longest continuous chain *that contains the carbonyl group*. Change the final *-e* in the name of the corresponding alkane to *-al*.

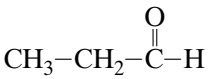
Following are three examples of correctly named aldehydes.



methanal



ethanal



propanal

Ketone Nomenclature

1. **Name the parent compound.** Locate the longest continuous chain *that contains the carbonyl group.* Change the final *-e* in the name of the corresponding alkane to *-one*.

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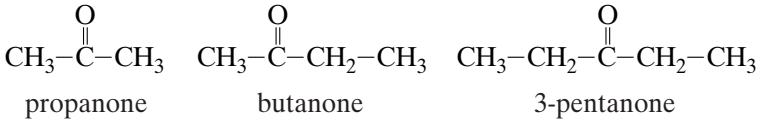
2. **Number the carbon atoms in the parent chain.** Number the carbon atoms in the chain so that the carbon atom in the carbonyl group has the lowest possible number.
3. **Insert position numbers.** Place the carbonyl position number in front of the name.
4. **Punctuate the name.** Separate the position number from the name with a hyphen.

Following are three examples of correctly named ketones.



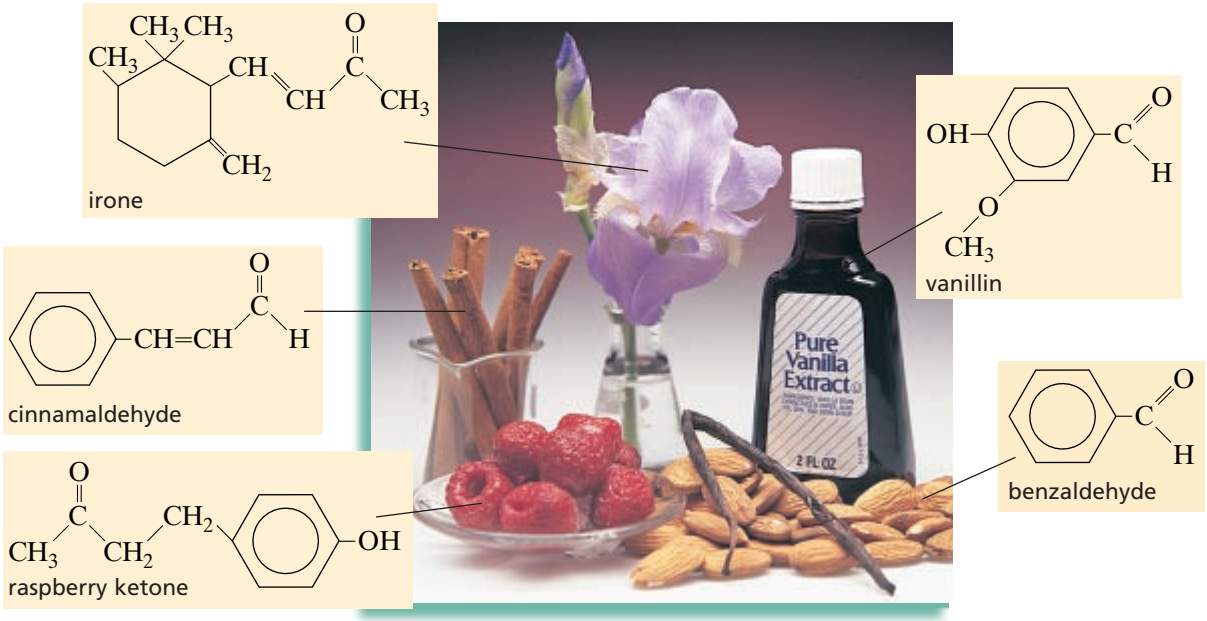
Properties and Uses of Aldehydes and Ketones

The simplest aldehyde is methanal, also known as formaldehyde. It was once commonly used in biology laboratories as a preservative for dead animals. Its most important commercial use, however, is in the production of plastics. One of the first commercial plastics, bakelite, was made by combining phenol and formaldehyde in a long chain.

The simplest ketone is propanone, whose common name is acetone. Acetone is found in some nail-polish removers because it dissolves the organic substances in nail polish. However, artificial fingernails are made of plastics that are also dissolved by acetone. Today other solvents are being used more frequently as nail-polish removers.

Aldehydes and ketones are often responsible for odors and flavors. For example, cinnamaldehyde contributes to the odor and flavor of cinnamon. Figure 21-4 gives some examples of odors and flavors that come from aldehydes and ketones.

FIGURE 21-4 Many common odors and flavors come from aldehydes and ketones.



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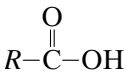
Carboxylic Acids

Carboxylic acids *are organic compounds that contain the carboxyl functional group.* The carboxyl group always comes at the end of a carbon-atom chain. A member of this class of organic compounds can be represented by the general formula shown below.

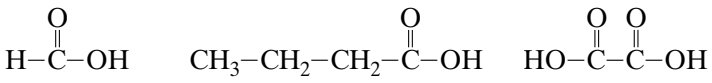


The rules for naming simple carboxylic acids are as follows.

Carboxylic Acid Nomenclature

Name the parent compound. Locate the longest continuous chain *that contains the carboxyl group.* If there is only one carboxyl group, change the final *-e* in the name of the corresponding alkane to *-oic acid*. If there is more than one carboxyl group, use the full name of the corresponding alkane, and add the suffix modified to indicate the number of carboxyl groups. For example, *-dioic acid* = 2, *-trioic acid* = 3, and so on.

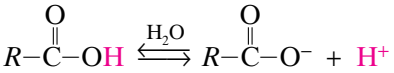
Following are three examples of correctly named carboxylic acids.



methanoic acid | butanoic acid | ethanedioic acid

Properties and Uses of Carboxylic Acids

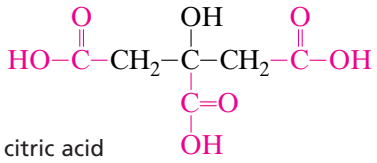
Carboxylic acids, like inorganic acids, react to lose a hydrogen ion and become a negatively charged ion in water.



Carboxylic acids are much weaker than many inorganic acids, such as hydrochloric, sulfuric, and nitric acids. Acetic acid, the weak acid in vinegar, is a carboxylic acid. The IUPAC name for acetic acid is ethanoic acid.

A number of carboxylic acids occur naturally in plants and animals. For example, citrus fruits, shown in Figure 21-5, contain citric acid. Table 21-5 lists more examples. Carboxylic acids are also used as food additives. For example, ethanoic and citric acids are used in foods to give them a tart or acidic flavor. Benzoic, propanoic, and sorbic acids are used as preservatives. All three acids kill microorganisms that cause foods to spoil.

The most widely used carboxylic acids are methanoic and ethanoic acids. Because they can be made inexpensively, they are the starting material for many chemical processes. For example, ethanoic acid is used in the production of polyvinyl acetate, PVA. PVA is used in latex paint, adhesives, and textile coatings.



citric acid

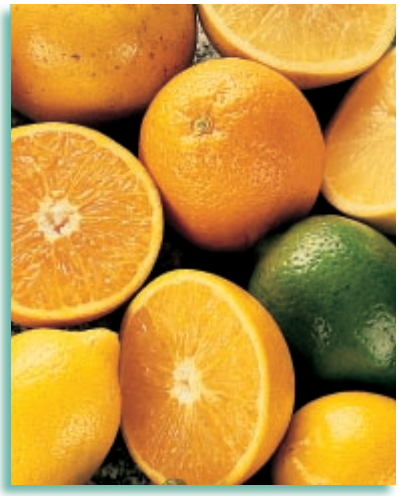


FIGURE 21-5 Citric acid, found in citrus fruits, contains three carboxylic acid groups shown in red on the structural formula.

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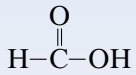
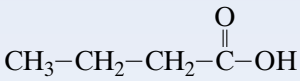
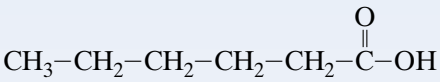
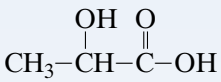
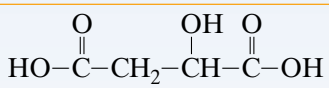
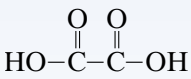
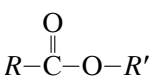
TABLE 21-5 Some Carboxylic Acids and Their Natural Sources

Carboxylic acid	Structural formula	Source
methanoic acid		ants
butanoic acid		rancid butter
hexanoic acid		milk fats, coconut oil, palm oil
lactic acid		sour milk, blood, and muscle fluid
malic acid		apples
oxalic acid		rhubarb

Esters

Esters *are organic compounds with carboxylic acid groups in which the hydrogen of the hydroxyl group has been replaced by an alkyl group.* The general formula for an ester is given below.

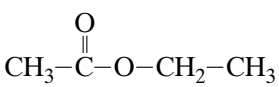


The IUPAC system for naming simple esters is as follows.

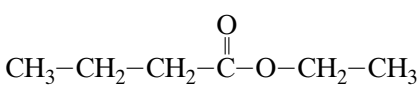
Ester Nomenclature

1. **Name the parent compound.** Name the carboxylic acid from which the ester was formed (see page 674). Change the *-oic acid* ending in the name of this acid to *-oate*. This gives the second half of the ester's name.
2. **Add the name of the alkyl group.** Identify and name the alkyl group that has replaced the hydrogen of the hydroxyl group. Add the name of the alkyl group to the front of the name.
3. **Leave appropriate spaces in the name.** There should be a space between the name of the alkyl group and the name of the parent compound.

Following are two examples of correctly named esters.



ethyl ethanoate



ethyl butanoate

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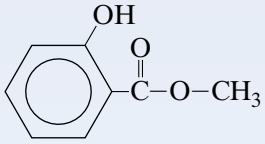
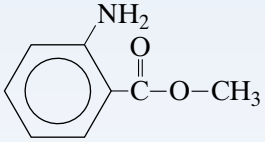
TABLE 21-6 Common Flavors and Odors Produced by Esters

Ester	Structural formula	Flavor or odor
ethyl butanoate	$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$	pineapple
methyl salicylate		wintergreen oil
geraniol formate	$H-\overset{\overset{O}{\|}}{C}-O-CH_2-CH=\overset{\overset{CH_3}{\|}}{C}-CH_2-CH_2-CH=\overset{\overset{CH_3}{\|}}{C}-CH_3$	rose
methyl anthranilate		grape juice and jasmine
linalyl acetate	$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{\|}}{\underset{\underset{CH=CH_2}{\|}}{C}}-CH_2-CH_2-CH=\overset{\overset{CH_3}{\|}}{C}-CH_3$	lavender

Properties and Uses of Esters

Esters are common in plants and are responsible for some distinctive flavors and odors. Table 21-6 lists some of these esters and the flavors and odors with which they are associated. At one time, compounds such as those listed in the table were obtained only from natural materials. But chemists have learned how to synthesize these and many other naturally occurring compounds for use as food additives. Figure 21-6 shows the structure of isoamyl acetate, which is found in bananas and is also used as an artificial flavoring.

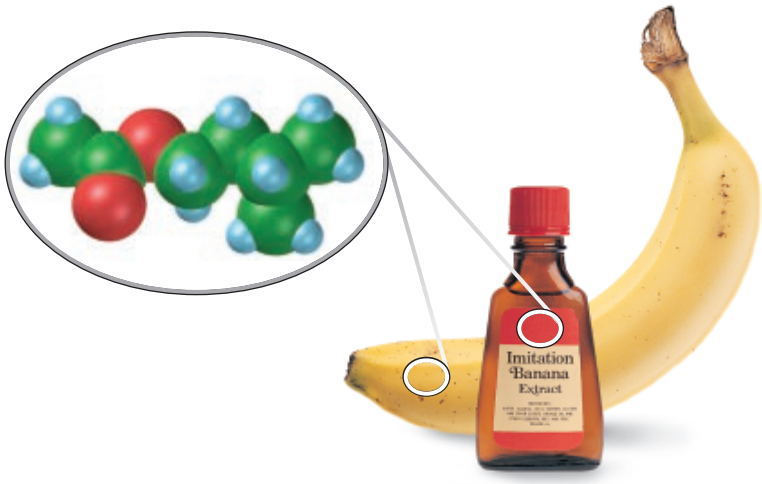


FIGURE 21-6 The ester in bananas can be synthesized and used as a flavoring.

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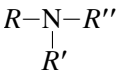
Amines

Amines *are organic compounds that can be considered to be derivatives of ammonia,* NH_3. They can be represented by the following general formula. Note that the functional group does *not* contain oxygen.

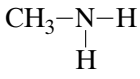


Amines are often named by a common system rather than the IUPAC system. The steps in naming a simple amine by the common system are as follows.

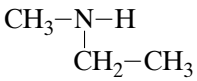
Amine Nomenclature

1. **Name the parent compound.** The end of the name will be *-amine*.
2. **Add the names of the alkyl groups.** Arrange the names of the alkyl groups attached to the nitrogen atom in alphabetical order. Add the prefixes *di-* or *tri-* in front of the group name if two or three, respectively, of the same kind are included in the amine. Combine these names in front of *-amine* to form one word.

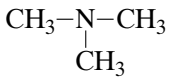
Following are three examples of correctly named amines.



methylamine
(primary amine)



ethylmethylamine
(secondary amine)

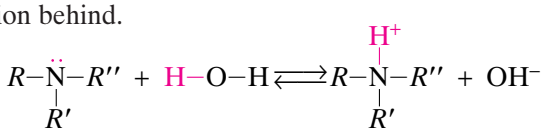


trimethylamine
(tertiary amine)

Amines are categorized as primary, secondary, or tertiary, depending on the number of hydrogen atoms of the ammonia molecule that have been replaced. As shown in the structures above, *in a* **primary amine,** *one hydrogen atom of an ammonia molecule has been replaced by an alkyl group. In a* **secondary amine,** *two hydrogen atoms of an ammonia molecule have been replaced by alkyl groups. In a* **tertiary amine,** *all three hydrogen atoms of an ammonia molecule have been replaced by alkyl groups.*

Properties and Uses of Amines

The chemical properties of the amines depend largely on the electronic structure of the nitrogen atom, which has an unshared pair of electrons. This region of negative charge makes amines weak bases in aqueous solutions. The unshared pair of electrons on the amine molecule attracts a positive hydrogen atom in a water molecule. The hydrogen atom bonds with the amine, forming a positively charged ion and leaving the hydroxide ion behind.



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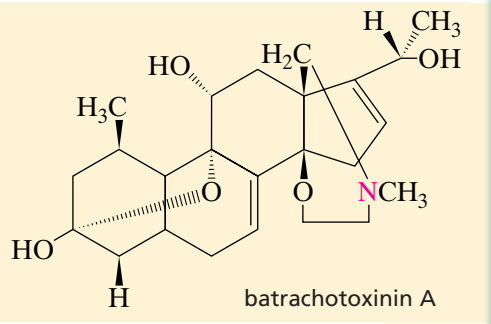


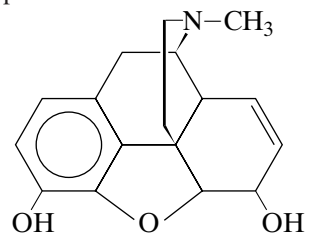
batrachotoxinin A

FIGURE 21-7 The poison dart frog produces toxic amines, one of which is batrachotoxinin A, that kill nerve cells. The nitrogen atom of the amine is shown in red.

An interesting example of this reaction involves two naturally occurring and toxic amines known as batrachotoxin and batrachotoxinin A. These compounds are produced by the poison dart frog, shown in Figure 21-7, which lives in the rain forests of Colombia. In water solution, both of these amines gain protons and become positively charged ions. Because these two amines carry the same charge as sodium ions found in the nervous system, they behave in much the same way. Both batrachotoxin ions can move through the openings in nerve cells, called sodium channels. These ions are much larger than sodium ions, however. They force the sodium channels to remain in the "open" position, and sodium ions are allowed to flood a nerve cell. This causes the nerve cell to continuously transmit nerve impulses, resulting in rapid death of the cell.

Amines are common in nature. They are often formed during the breakdown of proteins in animal cells. Two such amines are putrescine and cadaverine. Their names reflect their foul odors and presence in decaying bodies. Another amine, methylamine, has the unpleasant odor associated with dead fish. Yet a fourth amine, skatole, is found in feces and contributes to their odor.

The class of organic compounds known as alkaloids also consists of amines. *Alkaloids* are naturally occurring amine products of plants that have physiological effects on animals. Examples of alkaloids include caffeine, nicotine, morphine, and coniine (found in poisonous hemlock). Alkaloids tend to have complex chemical structures, as illustrated by the structure for morphine.



morphine (a tertiary amine)

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Table 21-7 summarizes the functional groups and the general formulas of the classes of organic compounds discussed in Sections 21-1 and 21-2.

TABLE 21-7 *Classes of Organic Compounds*

Class	Functional group	General formula
alcohol	$-OH$	$R-OH$
alkyl halide	$-X$ (X = F, Cl, Br, I)	$R-X$
ether	$-O-$	$R-O-R'$
aldehyde	$-\overset{\overset{O}{\|\|}}{C}-H$	$R-\overset{\overset{O}{\|\|}}{C}-H$
ketone	$-\overset{\overset{O}{\|\|}}{C}-$	$R-\overset{\overset{O}{\|\|}}{C}-R'$
carboxylic acid	$-\overset{\overset{O}{\|\|}}{C}-OH$	$R-\overset{\overset{O}{\|\|}}{C}-OH$
ester	$-\overset{\overset{O}{\|\|}}{C}-O-$	$R-\overset{\overset{O}{\|\|}}{C}-O-R'$
amine	$-\overset{\overset{\|}{}}{N}-$	$R-\overset{\overset{R'}{\|}}{N}-R''$

SECTION REVIEW

1. Give the general formula and class of organic compounds for each of the following:

a. $CH_3-CH_2-\overset{\overset{O}{\|\|}}{C}-OH$

b. $CH_3-\overset{\overset{O}{\|\|}}{C}-H$

c. $CH_3-CH_2-NH_2$

d. $CH_3-\overset{\overset{O}{\|\|}}{C}-O-CH_2-CH_3$

e. $CH_3-\overset{\overset{O}{\|\|}}{C}-CH_3$

2. Give the name of each of the following:

a. $CH_3-\overset{\overset{O}{\|\|}}{C}-CH_2-CH_2-CH_3$

b. $CH_3-CH_2-CH_2-\overset{\overset{O}{\|\|}}{C}-OH$

c. $CH_3-NH-CH_3$

3. Draw condensed structures for each of the following:
a. ethyl ethanoate
b. triethylamine
c. butanal

4. How are aldehydes and ketones alike? How do they differ from each other?

5. How do the strengths of organic acids compare with the strengths of most inorganic acids?

6. Show the reaction that occurs when amines are dissolved in water.

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Unraveling the Mystery of DNA

HISTORICAL PERSPECTIVE

Today genetic engineers can identify, modify, and even transplant genes, but virtually nothing was known about the chemical mechanism of heredity at the beginning of the twentieth century. The term* gene *was coined in 1909 to describe a molecule that existed only in theory at the time. By the century's midpoint, however, scientists were poised to discover the molecular structure of the gene and explain the biochemical process that is the foundation of modern genetics.

The Chemical Nature of the Gene

By the early part of the twentieth century, scientists knew that genes were one of two types of organic macromolecules: proteins or nucleic acids. Most researchers believed genes to be the former until 1944, when it was shown that hereditary information could be transmitted from one bacterial cell to another by DNA alone.

An Important New Technique

One problem early researchers encountered was the inability to directly observe the minuscule genes. The development of a relatively new crystallographic technique proved vital to the elucidation of the structures of DNA and other biological macromolecules.

The technique was called X-ray diffraction and involved shining X rays onto crystallized molecular samples to take "snapshots" of their structure. Until the 1950s, most X-ray crystallography was focused on proteins. But in 1951, James D. Watson realized the potential value of X-ray diffraction in determining a model for DNA. That year, he accepted a position at Cambridge University's Cavendish Laboratory to learn more about the procedure.

X-ray diffraction patterns of DNA taken by Rosalind Franklin were used to determine the structure of DNA.

A Fateful Union

At Cavendish, Watson befriended Francis Crick, a theoretical biophysicist. Crick did not know how to perform X-ray diffraction either, but he was adept at analyzing the images that resulted from it. Fortunately, Cavendish was also home to two experts on X-ray crystallography of DNA: Maurice Wilkins and Rosalind Franklin. With the help of these two experimentalists, Watson and Crick set out to solve the riddle of DNA.

A Big Leap

One of the team's biggest clues was the result of an investigation into proteins by Linus Pauling, the eminent chemist at the California Institute of Technology. Pauling determined the basic shape of a polypeptide chain, or protein strand, to be an α-helix, a large molecule of repeating units that twist around a central axis.

This discovery inspired Watson and Crick to look for a similar but more complex structure in DNA. Watson wrote:

> *In the α-helix, a single polypeptide . . . chain folds up into a helical arrangement held*

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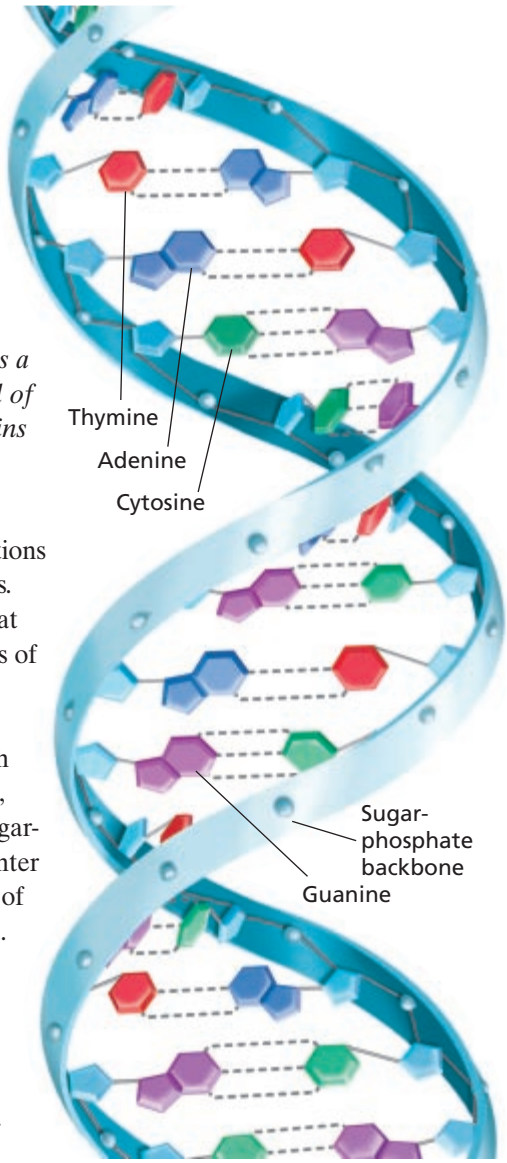
together by hydrogen bonds between groups on the same chain. Maurice told Francis, however, that the diameter of the DNA molecule was thicker than would be the case if only one polynucleotide (DNA strand) were present. This made him think that the DNA molecule was a compound helix composed of several polynucleotide chains twisted about each other.

Watson and Crick began contemplating DNA configurations with two, three, and four helices. They correctly hypothesized that the sugar and phosphate groups of DNA's basic repeating units, or nucleotides, alternated to form the molecular backbone of each helix in the molecule. However, they mistakenly situated the sugar-phosphate backbones in the center of the molecule, with the bases of the nucleotides jutting outward.

The DNA Solution

Redirected by new X-ray diffraction data obtained by Franklin, Watson began considering models with the sugar-phosphate chains on the outside of the DNA molecule and the bases pointing inward. After reviewing a titration study of DNA indicating that many, if not all, of the molecule's bases formed hydrogen bonds with each other, he speculated:

> *Conceivably the crux of the matter was a rule governing hydrogen bonding between bases. . . . I thus started wondering whether each DNA molecule consisted of two chains with identical base sequences held together by hydrogen bonds between pairs of identical bases.*



The Watson-and-Crick model of DNA contains opposing adenine-thymine and guanine-cytosine bases on a double-helical sugar-phosphate backbone.

Crick immediately observed that this like-with-like double-stranded model did not satisfy the symmetry requirements of the X-ray data. When Watson began exploring models pairing different bases, he uncovered the final clue to the DNA mystery:

> *. . . an adenine-thymine pair held together by two hydrogen bonds was identical in shape to a guanine-cytosine pair held together by at least two hydrogen bonds.*

Fitting the opposing adenine-thymine and guanine-cytosine bases inside the double-helical sugar-phosphate backbones resulted in the first correct molecular model of DNA, for which they were awarded a Nobel Prize in 1962.

A Long-Standing Theory

The model of DNA discovered by James Watson and Francis Crick has continued to be the basis of biochemical genetics. The model has enabled scientists to explain genetic mutations, to predict or correct certain genetic disorders, and to genetically engineer organisms to have desirable traits.

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SECTION 21-3

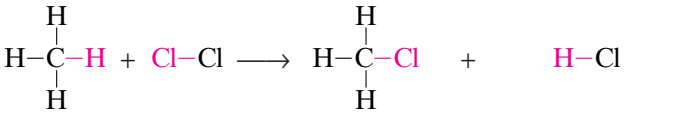
Organic Reactions

Objectives

- Describe and distinguish between the organic reactions: substitution, addition, condensation, and elimination.
- Relate some functional groups to some characteristic reactions.

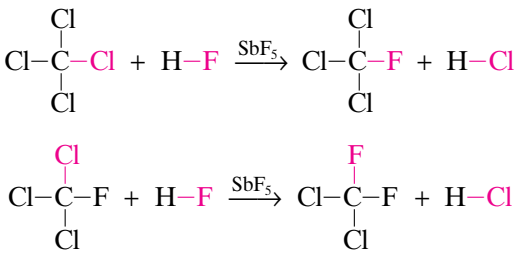
Substitution Reactions

A **substitution reaction** *is one in which one or more atoms replace another atom or group of atoms in a molecule.* The reaction between an alkane, such as methane, and a halogen, such as chlorine, to form an alkyl halide is an example of a substitution reaction. Notice that in this reaction, a chlorine atom replaces a hydrogen atom on the methane molecule.



methane chlorine chloromethane hydrogen chloride

Additional compounds can be formed by replacing the other hydrogen atoms remaining in the methane molecule. The products are dichloromethane, trichloromethane, and tetrachloromethane. Trichloromethane is also known as chloroform, and tetrachloromethane is also known as carbon tetrachloride. CFCs are formed by further substitution reactions between chloroalkanes and HF.



CHEMISTRY INTERACTIVE TUTOR
Module 7: Equilibrium

Addition Reactions

An **addition reaction** *is one in which an atom or molecule is added to an unsaturated molecule and increases the saturation of the molecule.* A common type of addition reaction is hydrogenation. In *hydrogenation,* one or more hydrogen atoms are added to an unsaturated molecule. Vegetable oils contain unsaturated fatty acids, long chains of carbon atoms with many double bonds. The following equation shows just one portion of an oil molecule. When hydrogen gas is blown through an oil, hydrogen atoms may add to the double bonds in the oil molecule.

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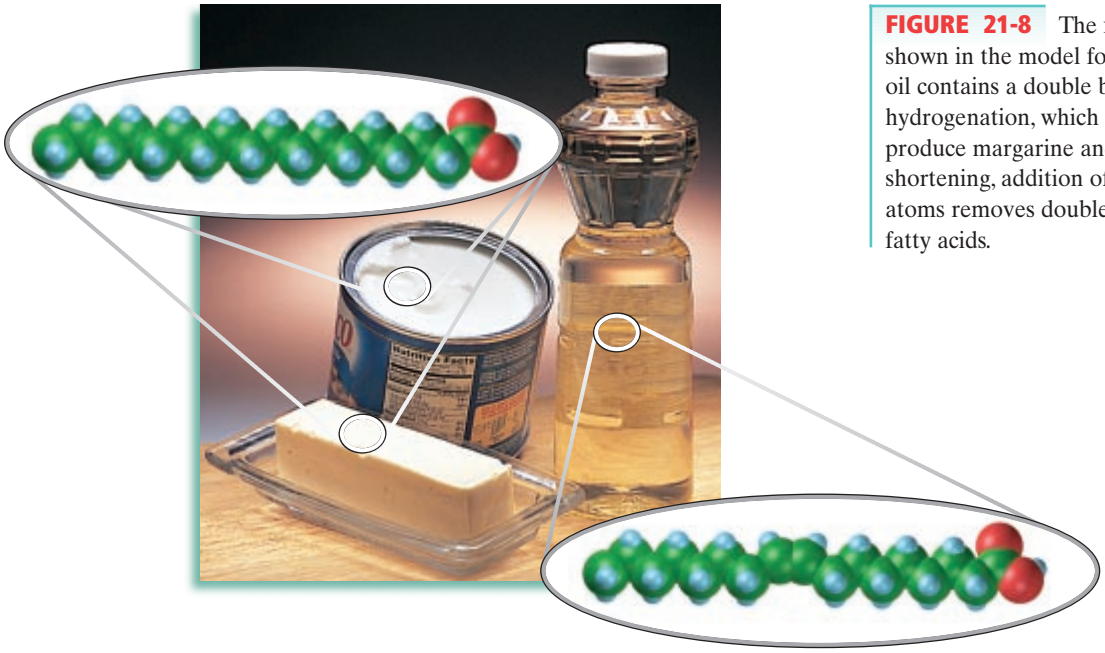
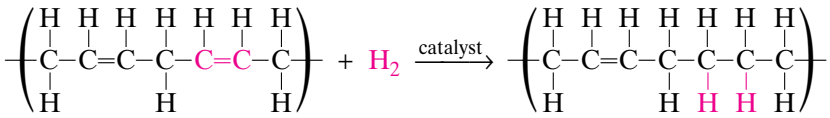


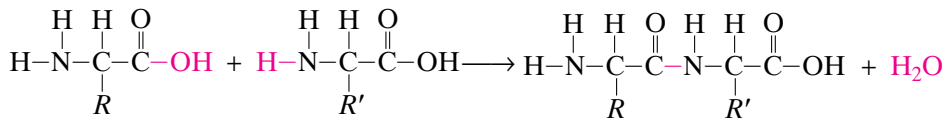
FIGURE 21-8 The fatty acid shown in the model for vegetable oil contains a double bond. During hydrogenation, which is used to produce margarine and vegetable shortening, addition of hydrogen atoms removes double bonds from fatty acids.



The molecule still consists of long chains of carbon atoms, but it contains far fewer double bonds. The conversion of these double bonds to single bonds changes the material from an oil, which is a liquid, into a fat, which is a solid. When you see the word *hydrogenated* on a food product, you know that an oil has been converted to a fat by this process. Examples of an oil and hydrogenated fats are shown in Figure 21-8.

Condensation Reactions

A **condensation reaction** *is one in which two molecules or parts of the same molecule combine.* A small molecule, such as water, is usually removed during the reaction. An example is the reaction between two amino acids, which contain both amine and carboxyl groups. One hydrogen from the amine group of one amino acid combines with the hydroxyl from the carboxyl group of the other amino acid to form a molecule of water. When repeated many times, this reaction forms a protein molecule.



amino acid amino acid dipeptide water

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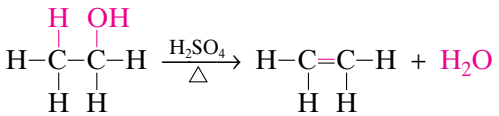
FIGURE 21-9 Sucrose is dehydrated when it reacts with concentrated sulfuric acid. Elimination of water produces a compound that is mostly carbon.

Elimination Reactions

An **elimination reaction** *is one in which a simple molecule, such as water or ammonia, is removed from adjacent carbon atoms of a larger molecule.* A simple example of an elimination reaction is the heating of ethanol in the presence of concentrated sulfuric acid. Under these conditions, a hydrogen atom bonded to one carbon atom and a hydroxyl group bonded to the second carbon atom are removed from the ethanol molecule. The hydrogen atom and hydroxyl group combine to form a molecule of water.



Another example of an elimination reaction is the dehydration of sucrose with concentrated sulfuric acid, shown in Figure 21-9.

SECTION REVIEW

1. Can an addition reaction occur between chlorine and ethane? Why or why not?
2. Does an addition reaction increase or decrease the saturation of a molecule?
3. What functional groups does the molecule of water come from in the condensation reaction between two amino acids?
4. Explain how elimination reactions could be considered the opposite of addition reactions.

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Polymers

SECTION 21-4

OBJECTIVES

- Explain the relationship between monomers and polymers.
- Describe how the differences in the general structures of linear, branched, and cross-linked polymers contribute to their properties.
- Identify the two main types of polymers and the basic reaction mechanisms by which they are made.
- Relate the structures of specific polymers to their properties and uses.

Polymers *are large molecules made of many small units joined to each other through organic reactions. The small units are* **monomers.** A polymer can be made from identical or different monomers. *A polymer made from two or more different monomers is a* **copolymer.**

Polymers are all around us. The foods we eat and clothes we wear are made of polymers. Some of the most common natural polymers include starch, cellulose, and proteins. Some synthetic polymers may be familiar to you as plastics and synthetic fibers.

Polymer Thermal Properties and Structure

Polymers can be classified by the way they behave when heated. *A* **thermoplastic polymer** *melts when heated and can be reshaped many times. A* **thermosetting polymer** *does not melt when heated but keeps its original shape.* The thermal properties of polymers can be explained by whether their structure is linear, branched, or cross-linked, as shown in Figure 21-10.

The molecules of a *linear polymer* are free to move. They slide back and forth against each other easily when heated. So, linear polymers are thermoplastic. The molecules of a *branched polymer* contain side chains that prevent the molecules from sliding across each other easily. However, branched polymers are still likely to be thermoplastic. In *cross-linked polymers,* adjacent molecules in the polymer have formed bonds with each other. Individual molecules are not able to slide past each other when heated. Cross-linked polymers retain their shape when heated and are thermosetting polymers.

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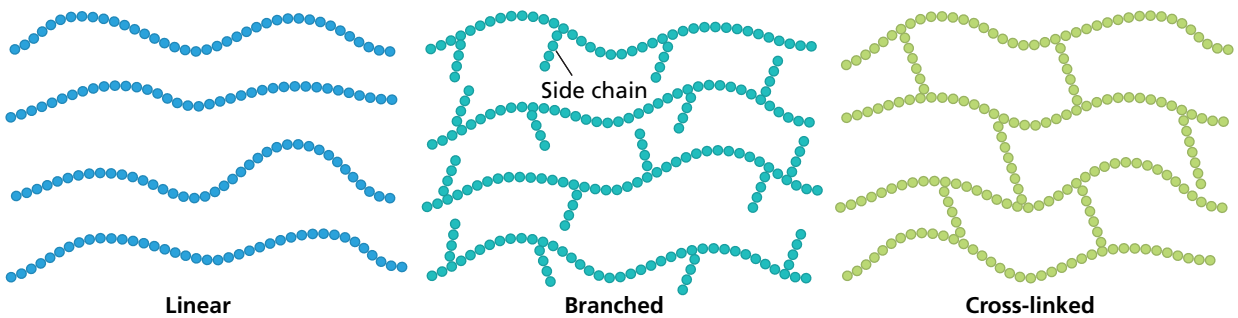

FIGURE 21-10 Compare structures of the three types of polymers. Linear polymers are free to slide. Branched and cross-linked polymers are inhibited.

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Addition Polymers

An **addition polymer** *is a polymer formed by chain addition reactions between monomers that contain a double bond.* For example, molecules of ethene can polymerize with each other to form polyethene, commonly called polyethylene.

$$\underset{\text{ethene}}{n\ CH_2{=}CH_2} \xrightarrow{\text{catalyst}} \underset{\text{polyethylene}}{{-}(CH_2{-}CH_2{-})_n}$$

The letter *n* shows that the addition reaction can be repeated multiple times to form a polymer *n* monomers long. In fact, this reaction can be repeated hundreds or thousands of times.

Forms of Polyethylene and Related Polymers

Various forms of polyethylene, shown in Figure 21-11, have different molecular structures. High-density polyethylene (HDPE) is a linear polymer. It has a high density because linear molecules can pack together closely. One use of HDPE is in plastic containers such as milk and juice bottles because HDPE tends to remain stiff and rigid.

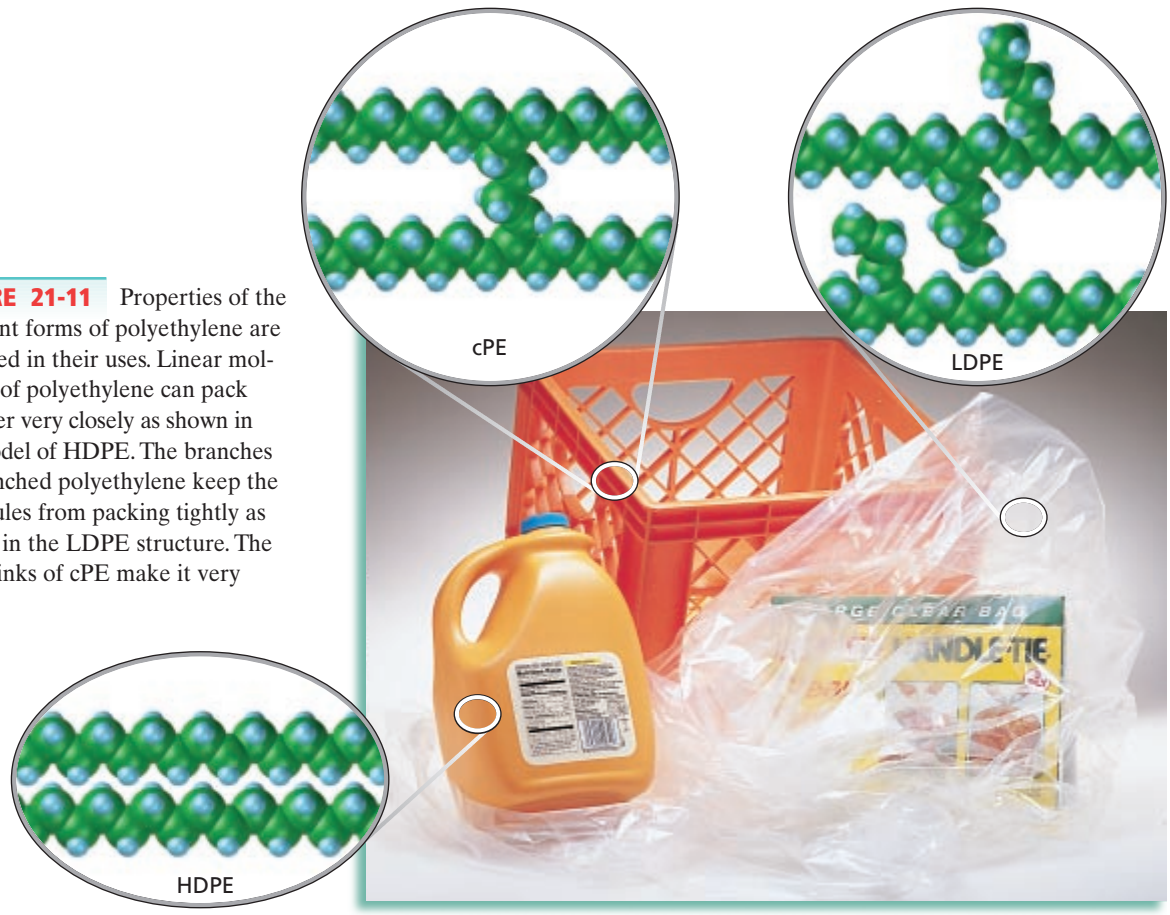

FIGURE 21-11 Properties of the different forms of polyethylene are reflected in their uses. Linear molecules of polyethylene can pack together very closely as shown in the model of HDPE. The branches of branched polyethylene keep the molecules from packing tightly as shown in the LDPE structure. The cross-links of cPE make it very strong.

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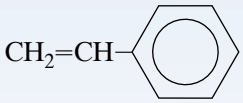
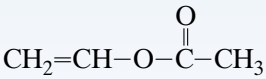
TABLE 21-8 *Some Addition Polymers*

Monomer structure	Monomer name	Polymer name	Typical use
$CH_2{=}CH{-}CH_3$	propylene	polypropylene	plastic bottles
$CH_2{=}CH{-}Cl$	vinyl chloride	polyvinyl chloride (PVC)	piping
$CH_2{=}CH{-}CN$	acrylonitrile	polyacrylonitrile	fabrics
	styrene	polystyrene	insulation
	vinyl acetate	polyvinyl acetate	adhesives, paints

If ethylene is heated to about 200°C at pressures above 200 atmospheres, random branching of the molecule chains may occur during polymerization. Branches form when hydrogen atoms are removed from the molecule and ethylene molecules add at these locations. Branched-chain molecules are not able to cluster as closely together as are linear molecules. Thus, the density of branched-chain polyethylene is less than that of linear polyethylene. The branched-chain form of polyethylene is known as low-density polyethylene (LDPE). LDPE tends to be less rigid than HDPE and is used, for example, in plastic bags.

When hydrogen atoms are removed from polyethylene molecules, two adjacent molecule chains may bond with each other. This forms a cross-link between the two molecules. Cross-linked polyethylene (sometimes called cPE) is even tougher and more rigid than HDPE. It is used for objects that need to be very strong.

Addition polymers similar to polyethylene can be made by substituting an atom or group of atoms for a hydrogen atom in ethene to form the monomer. Table 21-8 lists examples of these addition polymers.

Polystyrene, a polymer found in this table, is another example of a polymer whose properties can be altered. Pure polystyrene can be melted and molded for use in clear plastic cold-drink cups. Or it can be formed into tiny beads and then soaked in a low-boiling-point liquid, such as pentane. When this mixture is heated, the liquid vaporizes, expands, and forms tiny bubbles within the polystyrene. The product of this reaction is an opaque white material used to make hot-drink cups. Figure 21-12 shows the two types of polystyrene cups.

FIGURE 21-12 Both of these cups are made of polystyrene. Depending on how it is processed, polystyrene can be either flexible or rigid and brittle.

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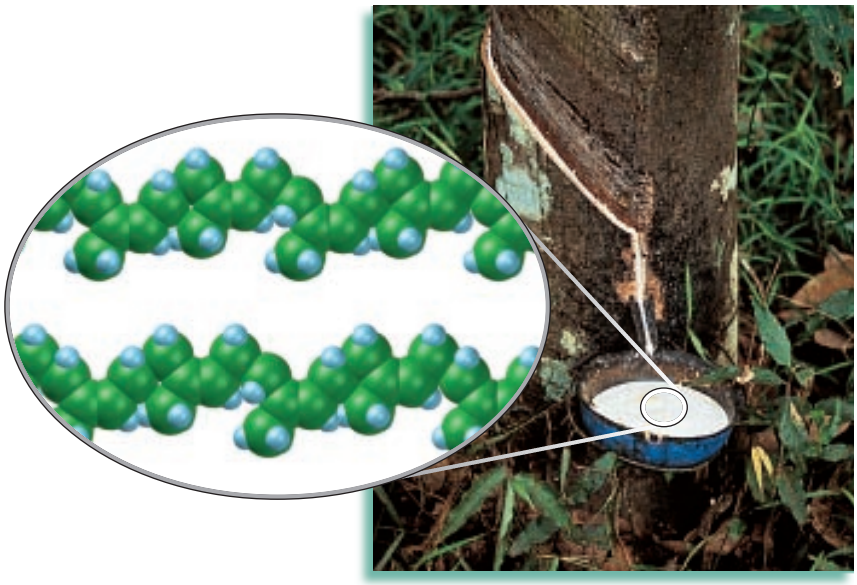
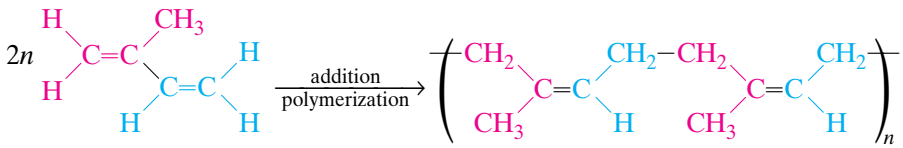


FIGURE 21-13 A rubber tree secretes latex, which is a suspension of rubber particles in water. When the rubber particles are precipitated, a gooey, sticky mass forms. An idealized model of natural rubber is shown in this figure.

Natural and Synthetic Rubber

Natural rubber is produced by the rubber tree, *Hevea brasiliensis,* shown in Figure 21-13. It is formed as the result of an addition reaction. The monomer in this reaction is 2-methyl-1,3-butadiene, commonly called isoprene.



isoprene polyisoprene

Natural rubber has relatively few practical applications. When warmed, individual molecules of polyisoprene slide easily back and forth past each other. The rubber gets soft and gooey, making it useless for many purposes.

A process for converting natural rubber into a useful commercial product was accidentally discovered by Charles Goodyear in 1839. Goodyear found that the addition of sulfur to molten rubber produces a material that remains very hard and tough when cooled. He called this process vulcanization. **Vulcanization** *is a cross-linking process between adjacent polyisoprene molecules that occurs when the molecules are heated with sulfur atoms.* Sulfur atoms bond to a carbon atom in one molecule and a second carbon atom in a second molecule, forming a cross-link between the two molecules. This is shown in the model in Figure 21-14. Vulcanization enabled rubber to be used in a wide variety of products, such as hoses, rainwear, and tires.

In the first year of World War II, Japan controlled large portions of Southeast Asia, where most of the world's natural rubber is obtained. The United States and other Allied nations were forced to develop

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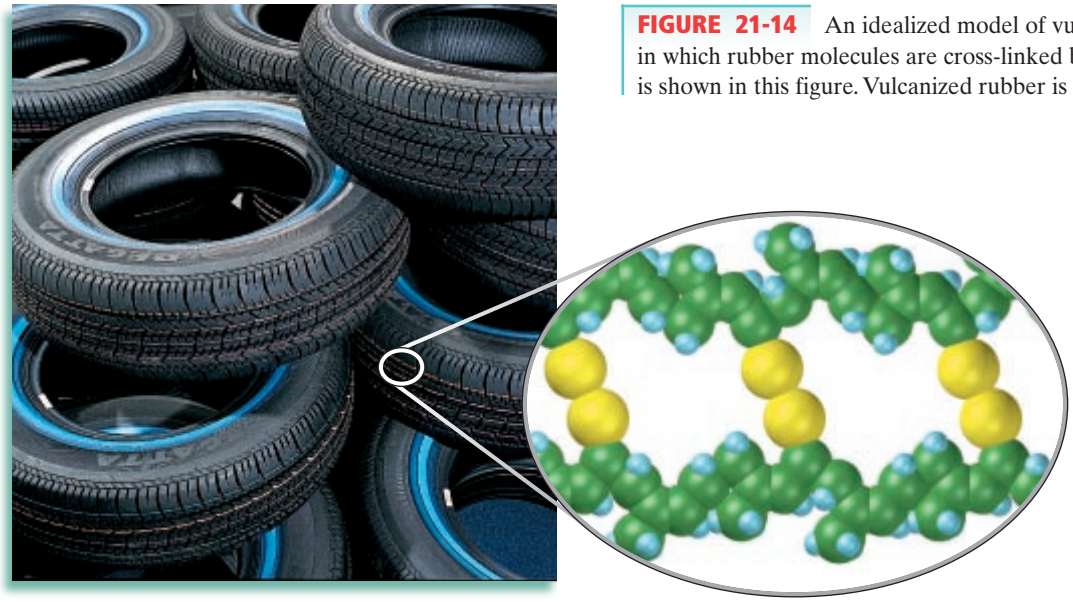
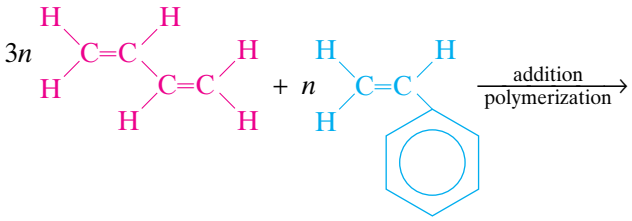
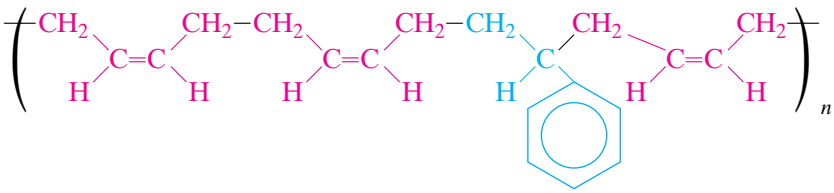


FIGURE 21-14 An idealized model of vulcanized rubber, in which rubber molecules are cross-linked by sulfur atoms, is shown in this figure. Vulcanized rubber is used in tires.

synthetic substitutes for natural rubber. Some synthetic rubbers have superior properties to natural rubber. Styrene-butadiene rubber, SBR, is a copolymer made in the reaction between styrene and butadiene, as shown below. SBR is used primarily in tires.

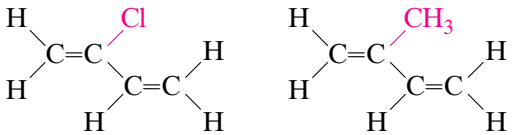


1,3-butadiene styrene



styrene-butadiene rubber (SBR)

Another substitute, neoprene, is formed during the polymerization of 2-chlorobutadiene. Notice that 2-chlorobutadiene is identical to isoprene, the monomer of natural rubber, except for the presence of a chlorine atom in place of a methyl group on the number 2 carbon atom.



2-chlorobutadiene

isoprene

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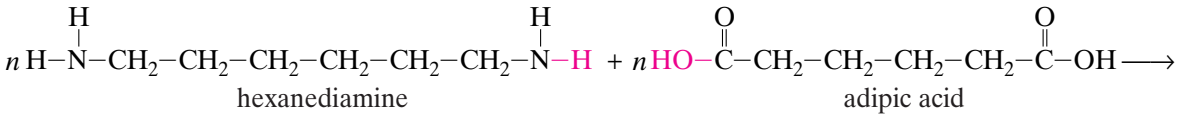
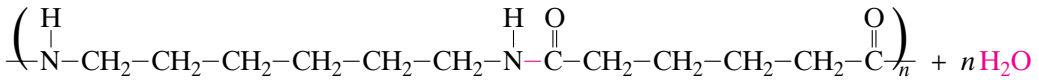
Condensation Polymers

A **condensation polymer** *is a polymer formed by condensation reactions.* Monomers of condensation polymers must contain two functional groups. This allows each monomer to link with two other monomers by condensation reactions. Condensation polymers are usually copolymers with two monomers in an alternating order.

Nylon and the Polyamides

One example of a condensation polymer is shown below. A carboxylic acid with two carboxyl groups, adipic acid, and an amine with two amine groups, hexanediamine, react with each other through the elimination of a molecule of water.





This reaction is shown in Figure 21-15. The product contains two kinds of monomers, the adipic acid monomer and the hexanediamine monomer. This copolymer is known as nylon 66 because each of the monomers contains six carbon atoms. Nylon 66 was invented by Dr. Wallace Carothers in 1935 and is one of the most widely used of all synthetic polymers.

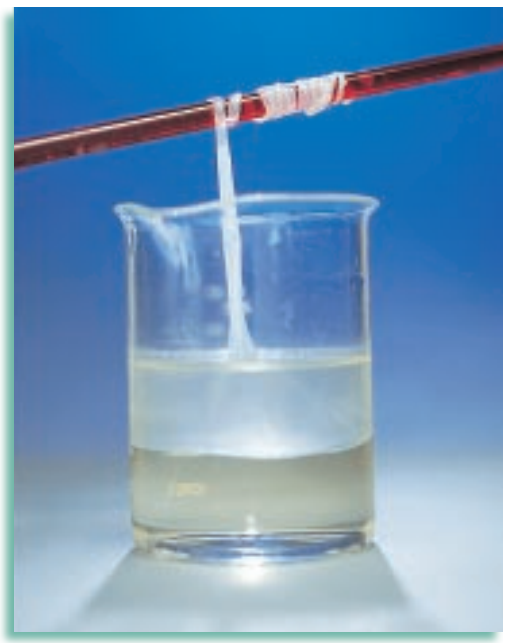


FIGURE 21-15 Nylon 66, shown here being wound onto a stirring rod, is produced from the polymerization of adipic acid (the top layer) and hexanediamine (the bottom layer).

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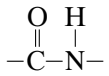
Nylon 66 is an example of a polyamide polymer. The word *polyamide* comes from the presence of the amide group in the polymer. The structure of the amide group is shown below.

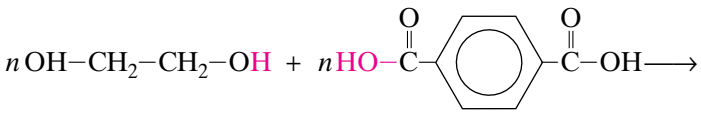


Polyamides have become commercial successes because they can be fabricated into so many different forms. For example, they can be knitted and woven, like natural fibers, to make stockings and other types of clothing. When polyamides are treated with radiation, extensive cross-linking occurs and the final product becomes very rigid and strong. One product made in this way, Kevlar, is so strong that it is used in the manufacture of bullet-proof vests used by police officers.

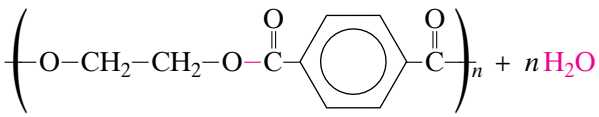
FIGURE 21-16 This thread is made from polyester.

Polyester

Polyesters are another common type of condensation polymer. Polyethylene terephthalate, PET, is a polyester formed when terephthalic acid reacts with ethylene glycol.



ethylene glycol terephthalic acid



PET water

PET has a vast range of uses, such as in tires, photographic film, food packaging, and bottles. Its best known use may be as a fiber called polyester, which is widely used in permanent-press clothing. Polyester fabric is made wrinkle resistant by the cross-linking of its polymer strands. Polyester thread is shown in Figure 21-16.

SECTION REVIEW

1. Would the handles of cookware more likely be made of a thermosetting polymer or a thermoplastic polymer? Why?
2. Would it be possible to have an addition polymer synthesized from a monomer that has only single bonds? Why or why not?
3. Make a simple diagram showing how the structure of a soft, pliable polyethylene differs from the structure of the form that is the most rigid and stiff.
4. Why can a molecule with only one functional group *not* undergo a condensation reaction to form a polymer?

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High-Barrier Plastics

Flat-tasting soda? Technology comes to the rescue. No matter how tightly the cap is sealed on a bottle, soda loses fizz over time. Because of the nature of plastic, the carbon dioxide gas actually escapes through the bottle. Benny Freeman, an associate professor of chemical engineering at North Carolina State University, has discovered how to stop this problem with a special kind of plastic called a liquid crystalline polymer.

According to Freeman, the long molecules that make up plastics do not fit together tightly. Instead, the plastic molecules are constantly moving and opening gaps between them similar to the spaces between noodles in a bowl of cooked spaghetti. Gas molecules can pass through these gaps. In a soda bottle, the carbon dioxide in the soft drink dissolves into the plastic and escapes into the air outside the bottle. Conversely, plastic containers also allow oxygen to seep inside them, which can spoil the food they hold.

Liquid crystal polymers, or LCPs, are made up of long molecules, like other plastics are. But, says Freeman, the molecules in an LCP are much straighter, and they all point in the same general direction. Instead of looking like a bowl of cooked pasta, LCP molecules more closely resemble a box of uncooked spaghetti packed tightly together. Because it is much more difficult for gas molecules to squeeze through them, LCPs make an ideal material for manufacturing containers.

The LCP layer (white) of this power cable makes the cable waterproof.

Aside from keeping soft drinks fresh, these high-barrier plastics could also replace glass packaging for foods that easily become stale or spoiled from contact with oxygen. That would result in much lighter, unbreakable containers. Gas tanks made from LCPs would better prevent harmful fumes from leaking out and polluting the environment. The liquid crystal polymer could also be used as a protectant to line underground electrical cables, making them virtually waterproof and corrosion-free. LCPs are currently used to line the breathing system of NASA's new spacesuits.

Liquid crystal polymers have not yet made it into the packaging of everyday products because they are several times more expensive than regular plastics. Freeman thinks that this problem could be solved by creating what he calls a composite structure: a combination of regular plastic and the liquid crystal polymer. By sandwiching a thin LCP layer between two pieces of regular plastic, manufacturers could keep their costs down and still keep your soda fizzy.

"We are," says Freeman, "at the beginning of really understanding where you can start to manipulate structure and actually control properties in these materials. There's still a lot of uncharted territory in the science of these materials."

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Back

CHAPTER 21 REVIEW

CHAPTER SUMMARY

21-1

- A functional group is an atom or group of atoms responsible for the properties of the organic compound which contains the functional group.
- Systematic names of organic compounds indicate the type and position of functional groups present.
- Alcohols contain the hydroxyl functional group. Their tendency to form hydrogen bonds affects their properties and uses.
- In alkyl halides, one or more hydrogen atoms of an alkane have been replaced by one or more halogen atoms. One class of alkyl halides, the CFCs, has many important industrial uses but may cause serious environmental problems.
- Two alkyl groups are joined to an oxygen atom in ethers. Generally unreactive, they are widely used as solvents.
- The physical and chemical properties of organic classes often reflect the ability or inability of molecules in each class to form hydrogen bonds.

Vocabulary

alcohols (663) alkyl halides (666) ethers (669) functional group (663)

21-2

- Aldehydes and ketones both contain the carbonyl group and are responsible for some odors and flavors. In aldehydes, the carbonyl group is attached to the first carbon atom of a carbon-atom chain. In ketones, it is in the middle of a carbon-atom chain.
- Carboxylic acids contain carboxyl groups. They act as weak acids in aqueous solutions.
- In esters, the hydrogen atom of a carboxylic acid group has been replaced with an alkyl group. Natural and synthetic esters give many foods their flavors and odors.
- Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by one or more alkyl groups. They behave as weak bases in aqueous solutions.

Vocabulary

aldehydes (672) carboxylic acids (674) ketones (672) secondary amine (677)
amines (677) esters (675) primary amine (677) tertiary amine (677)

21-3

- Both addition and substitution reactions add atoms to a molecule. In substitution reactions, an atom or group of atoms is replaced. In addition reactions, an atom or group of atoms is added to a double or triple bond.
- A small molecule is usually removed during both condensation reactions and elimination reactions. In a condensation reaction, two molecules or parts of the same molecule combine. In an elimination reaction, a large molecule eliminates a small molecule.

Vocabulary

addition reaction (682) condensation reaction (683) elimination reaction (684) substitution reaction (682)

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CHAPTER SUMMARY continued

21-4

- Polymers are large molecules made of many repeating units called monomers. A copolymer consists of two or more different monomers.
- Thermosetting polymers cannot be melted once they are formed. Thermoplastic polymers can be melted more than once.
- The physical properties of polymers are strongly influenced by the presence or absence of branching and cross-linking among polymer chains.
- Addition reactions require that the monomers contain a double bond. Polyethylene and related polymers as well as natural and synthetic rubbers involve addition polymerization.
- Monomers of condensation polymers must contain two functional groups. Nylon 66, other polyamides, and polyesters are condensation polymers.

Vocabulary

addition polymer (686)
condensation polymer (690)
copolymer (685)
monomers (685)
polymers (685)
thermoplastic polymer (685)
thermosetting polymer (685)
vulcanization (688)

REVIEWING CONCEPTS

1. Write the general formula for each of the following:
a. alcohol
b. ether
c. alkyl halide (21-1)

2. Based on the boiling points of water and methanol, in which would you expect to observe a greater degree of hydrogen bonding? Explain your answer. (21-1)

3. a. Why is glycerol used in moisturizing skin lotions?
b. How does this relate to the chemical structure of glycerol? (21-1)

4. State two advantages and one disadvantage of using gasohol as an automotive fuel. (21-1)

5. Why are CFCs regarded as an environmental hazard? (21-1)

6. Alcohols and ethers are both organic compounds that contain oxygen. Explain how their chemical structures differ. (22-1)

7. What is the important chemical property of ethers that leads to their most common use? (21-1)

8. Write the general formula for each of the following:
a. aldehyde
b. ketone
c. carboxylic acid
d. ester
e. amine (21-2)

9. Aldehydes and ketones both contain the same functional group. Why are they classified as separate classes of organic compounds? (21-2)

10. a. Cinnamaldehyde is responsible for what odor?
b. The IUPAC name for cinnamaldehyde is 3-phenyl-2-propenal. Based on its names, to which class of compounds does it belong? (21-2)

11. Why can a carboxyl group not be in the middle of a carbon-atom chain? (21-2)

12. a. Show the reaction that occurs when carboxylic acids are dissolved in water.
b. What property of carboxylic acids does this reaction illustrate? (21-2)

13. How are esters related to carboxylic acids? (21-2)

14. What element do amines contain besides carbon and hydrogen? (21-2)

15. Explain why an amine acts as a base. (21-2)

16. Show the reaction that occurs when aqueous solutions of carboxylic acids and amines are mixed. (21-2)

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17. Name five classes of organic compounds that are often responsible for odors and flavors. (21-2)

18. What classes of organic compounds contain oxygen? (21-1 and 21-2)

19. What type of chemical reaction would you expect to occur between 2-octene and hydrogen bromide, HBr? (21-3)

20. How many molecules of chlorine, Cl_2, can be added to a molecule of 1-propene? a molecule of 1-propyne? (21-3)

21. Compare substitution and addition reactions. (21-3)

22. What problems would you expect to encounter in trying to hydrogenate hexane, C_6H_{14}? (21-3)

23. In a chemical reaction, two small molecules are joined and a water molecule is produced. What type of reaction took place? (21-3)

24. Do elimination reactions increase or decrease the saturation of a molecule? (21-3)

25. Name three common natural products and three synthetic products made of polymers. (21-4)

26. Some automobile engine parts are made of polymers. Do you think these polymers are thermosetting or thermoplastic? Explain your answer. (21-4)

27. Classify each of the following as thermosetting or thermoplastic:
a. linear polymer
b. branched polymer
c. cross-linked polymer (21-4)

28. What are two reactions by which polymers can be formed? (21-4)

29. What is the structural requirement for a molecule to be a monomer in an addition polymer? (21-4)

30. Explain the structural molecular differences between the following three types of polyethylene: HDPE, LDPE, and cPE. (21-4)

31. What is the primary structural difference between polyethylene and polystyrene? (21-4)

32. Give a molecular explanation for the fact that natural rubber melts when it is heated but vulcanized rubber does not. (21-4)

33. How is the molecular structure of neoprene different from that of natural rubber? (21-4)

34. Could ethanoic acid be used as a monomer in a condensation polymer? Why or why not? (21-4)

35. Draw the structural formula for the amide group. (21-4)

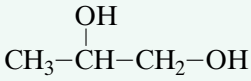
36. Why is polyester wrinkle resistant? (21-4)

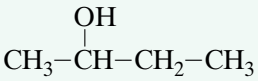
PROBLEMS

Organic Compound Nomenclature

37. Name the following alcohols:

a. CH_3-OH

b.


c.


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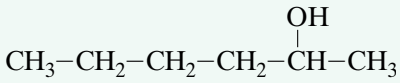
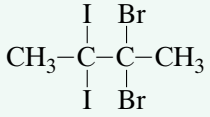


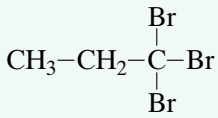
38. Draw condensed structures for each of the following alcohols:
a. 2,3-pentanediol
b. 1-pentanol
c. 1,2,3-propanetriol
d. ethanol

39. Name the following alkyl halides. (Hint: See Sample Problem 21-1.)

a. CH_3-I

b. $Cl-CH_2-CH_2-Cl$

c.


d.


40. Draw condensed structures for each of the following alkyl halides:
a. 2,3,4-trichloropentane
b. 1,1-diiodopropane
c. 1-fluorohexane
d. 2,2-dichloro-1,1-difluoropropane

41. Name the following ethers. (Hint: See Sample Problem 21-2.)

a. $CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$

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b. $CH_3-O-CH_2-CH_3$

c. $CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH_3$

d. $CH_3-CH_2-O-CH_2-CH_2-CH_2-CH_3$

42. Draw condensed structures for each of the following ethers:

a. dimethyl ether
b. methyl propyl ether
c. butyl propyl ether
d. ethyl heptyl ether

43. Name the following aldehydes:

a. $CH_3-\overset{\overset{O}{\|}}{C}-H$

b. $CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

c. $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

d. $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

44. Draw condensed structures for each of the following aldehydes:

a. methanal
b. hexanal
c. octanal
d. ethanal

45. Name the following ketones:

a. $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

b. $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

c. $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

d. $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

46. Draw condensed structures for each of the following ketones:

a. 3-hexanone
b. 2-pentanone
c. 2-octanone
d. 2-hexanone

47. Name the following carboxylic acids:

a. $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

b. $CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

c. $H-\overset{\overset{O}{\|}}{C}-OH$

d. $HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

48. Draw condensed structures for each of the following carboxylic acids:

a. butanoic acid
b. hexanoic acid
c. hexanedioic acid
d. heptanoic acid

49. Name the following esters:

a. $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$

b. $H-\overset{\overset{O}{\|}}{C}-O-CH_3$

c. $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

d. $CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

50. Draw condensed structures for each of the following esters:

a. butyl ethanoate
b. ethyl methanoate
c. propyl propanoate
d. methyl butanoate

51. Name the following amines:

a. CH_3-NH_2

b. $CH_3-CH_2-NH-CH_2-CH_3$

c. $CH_3-CH_2-NH-CH_3$

d. $CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$

52. Draw condensed structures for each of the following amines:

a. butylmethylamine
b. ethylamine
c. diethylmethylamine
d. ethylpropylamine

Organic Reactions

53. Which of the following reactions is a substitution reaction?

a. $CH_2=CH_2 + Cl_2 \longrightarrow Cl-CH_2-CH_2-Cl$

b. $CH_3-CH_2-CH_2-CH_3 + Cl_2 \longrightarrow Cl-CH_2-CH_2-CH_2-CH_3 + HCl$

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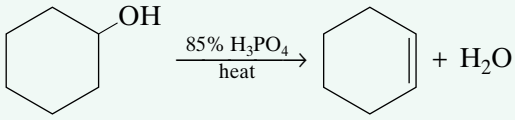
c. $CH_3{-}OH + CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH \longrightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + H_2O$

54. Which of the following reactions is an addition reaction?

a. $CH_3{-}CH_2{-}CH{=}CH_2 + Br_2 \longrightarrow CH_3{-}CH_2{-}\underset{\underset{Br}{|}}{CH}{-}CH_2{-}Br$

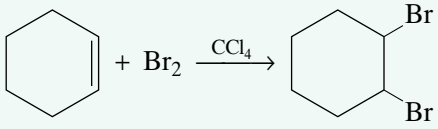
b. 

$+ H_2O$

c. $CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH + CH_3{-}OH \longrightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + H_2O$

55. Which of the following reactions is a condensation reaction?

a. $CH_3C{\equiv}CH + HBr \xrightarrow{\text{ether}} CH_3{-}\overset{\overset{Br}{|}}{C}{=}CH_2$

b. 

c. $CH_3{-}CH_2{-}OH + CH_3{-}CH_2{-}OH \xrightarrow{H_2SO_4} CH_3{-}CH_2{-}O{-}CH_2{-}CH_3 + H_2O$

56. Which of the following reactions is an elimination reaction?

a. $CH_2{=}CH{-}CH_2{-}CH_3 + Cl_2 \longrightarrow Cl{-}CH_2{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}CH_3$

b. $CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 \xrightarrow{H_3O^+} CH_3{-}CH{=}CH_2 + H_2O$

c. $CH_3CH_3 + Cl_2 \xrightarrow[\text{heat}]{\text{light or}} CH_3CH_2Cl + HCl$

Calculations with Organic Compounds

57. Calculate the molecular mass of trichlorofluoromethane.

58. A compound is found to contain 54.5% carbon, 9.1% hydrogen, and 36.4% oxygen.
a. Determine the simplest formula.
b. The molecular mass of this compound is 88.1 g. What is the molecular formula?

59. The hydronium ion concentration in 0.05 M acetic acid is 9.4×10^{-4} mol/L. What is the pH of the solution?

60. What volume of ethanol must be diluted with water to prepare 500. mL of 0.750 M solution? The density of ethanol is given as 0.789 g/mL.

61. 1,2-ethanediol, also called ethylene glycol, is commonly used as an antifreeze. The density of ethylene glycol is 1.432 g/mL.
a. Calculate the theoretical freezing point of the water in a 50% (by volume) solution of ethylene glycol.
b. The actual freezing point of such a solution is about –37°C. Account for any difference between this and the value you calculated.

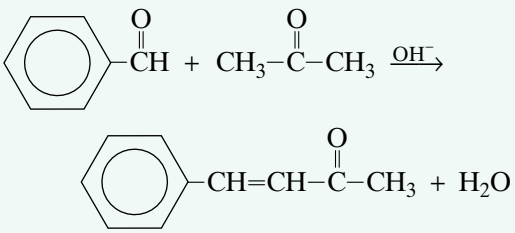
MIXED REVIEW

62. Classify each of the following reactions as an elimination reaction or a condensation reaction:

a. $CH_3{-}\overset{\overset{Br}{|}}{C}{=}CH_2 + NaNH_2 \longrightarrow CH_3C{\equiv}CH + NaBr + NH_3$

b. $CH_3{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 \xrightarrow[\text{heat}]{85\%\ H_3PO_4} CH_3{-}CH{=}CH{-}CH_3 + H_2O$

c. $CH_3{-}CH_2{-}OH + CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH \longrightarrow CH_3{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + H_2O$

d. 

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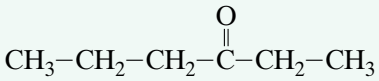
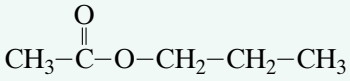
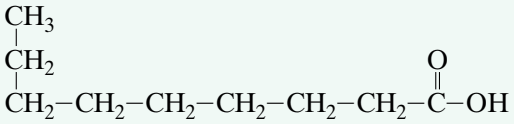
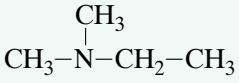
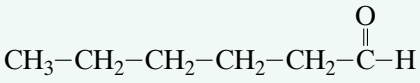
63. Name the following compounds:

a. 

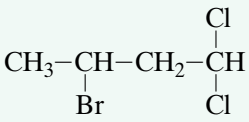
b. 

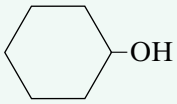
c. 

d. 

e. 

f. $CH_3-CH_2-O-CH_2-CH_2-CH_3$

g. 

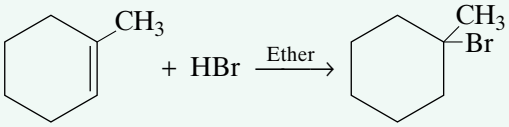
h. 

64. Classify each of the following reactions as a substitution reaction or an addition reaction:

a. $CH_3-CH_2-CH_2-CH_2-OH + HCl \xrightarrow[\text{heat}]{ZnCl_2} CH_3-CH_2-CH_2-CH_2-Cl + H_2O$

b. $CH_2=CH_2 + HBr \xrightarrow[25°C]{\text{Ether}} CH_3-CH_2-Br$

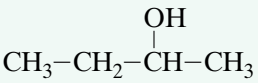
c. $CH\equiv CH + HCl \xrightarrow{HgCl_2} CH_2=CH-Cl$

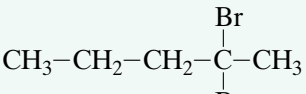
d. 

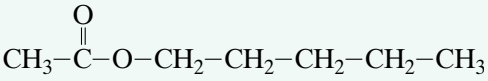
65. Draw structural formulas for each of the following compounds:

a. 1,2,3-trichloropropane
b. 1-butanol
c. ethyl methyl ether
d. propanoic acid
e. methyl propanoate
f. trimethylamine

66. For each of the following, determine if the compound is named correctly. If it is not, give the correct name.

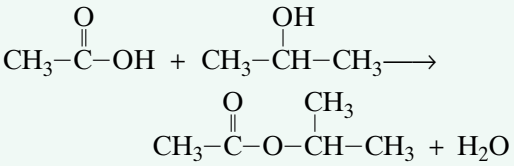
a. 
2-butanol

b. 
4-dibromopentane

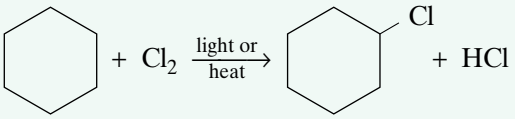
c. 
ethyl pentanoate

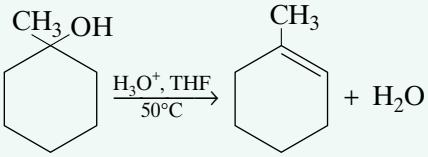
d. $CH_3-NH-CH_2-CH_2-CH_3$
methylpropylamine

67. Identify each of the following reactions as an addition, substitution, elimination, or condensation reaction:

a. 

b. $CH_2=CH-CH_3 + Cl_2 \longrightarrow Cl-CH_2-CH(Cl)-CH_3$

c. 

d. 

CRITICAL THINKING

68. Applying Ideas How does ethylene glycol protect radiator fluid in an automobile from both freezing in the winter and boiling over in the summer?

69. Predicting Outcomes Would a collection of 1,2-ethanediol molecules be likely to form twice as many hydrogen bonds as an equal number of ethanol molecules? Why or why not?

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TECHNOLOGY & LEARNING

70. Graphing Calculator Predict the Freezing Point

The graphing calculator can run a program that predicts the freezing point of ethylene glycol solutions, given the concentration. Begin by creating a table of data. Use the program to carry out the predictions.

Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data and run the application as directed. If you are using another calculator, your teacher will provide you with keystrokes and data sets to use. Remember that after creating your lists, you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

a. What is the approximate freezing point of the solution with a molality of 5.00m?
b. What is the approximate freezing point of the solution with a molality of 10.00m?
c. What is the approximate freezing point of the solution with a molality of 13.00m?

RESEARCH & WRITING

71. A class of CFCs known as hydrochlorofluorocarbons (HCFCs) has been suggested as a substitute for CFCs in many applications. How does the chemical structure of an HCFC differ from that of a CFC? Why are the HCFCs more acceptable environmentally than other CFCs?

72. At one time, a group of compounds known as the PCBs were very popular for a number of industrial applications. Find out the general structural formula for these compounds and the properties that made them so popular. Also find out why the PCBs were eventually banned for most industrial uses.

73. The widespread use of synthetic polymers in modern society has created a number of new environmental problems. Find out what some of these problems are and what can be done to reduce them.

ALTERNATIVE ASSESSMENT

74. Performance Devise a set of experiments to study how well biodegradable plastics break down. If your teacher approves your plan, conduct a class experiment to test the procedure on products labeled "biodegradable."

75. Performance Your teacher will make available unlabeled samples of benzoic acid, ethyl alcohol, and hexanediamine. Develop an experiment to identify each. If your teacher approves your plan, identify the unknown substances.

76. Keep a list of the food you consume in a single day. Compare the content labels from those foods, and then list the most commonly used chemicals in them. With the aid of your teacher and some reference books, try to classify the organic chemicals by their functional groups.

77. As a class or small group, research the preservatives used in various foods. Examine their chemical structure. Determine a way to test for organic functional groups of possibly hazardous preservatives.

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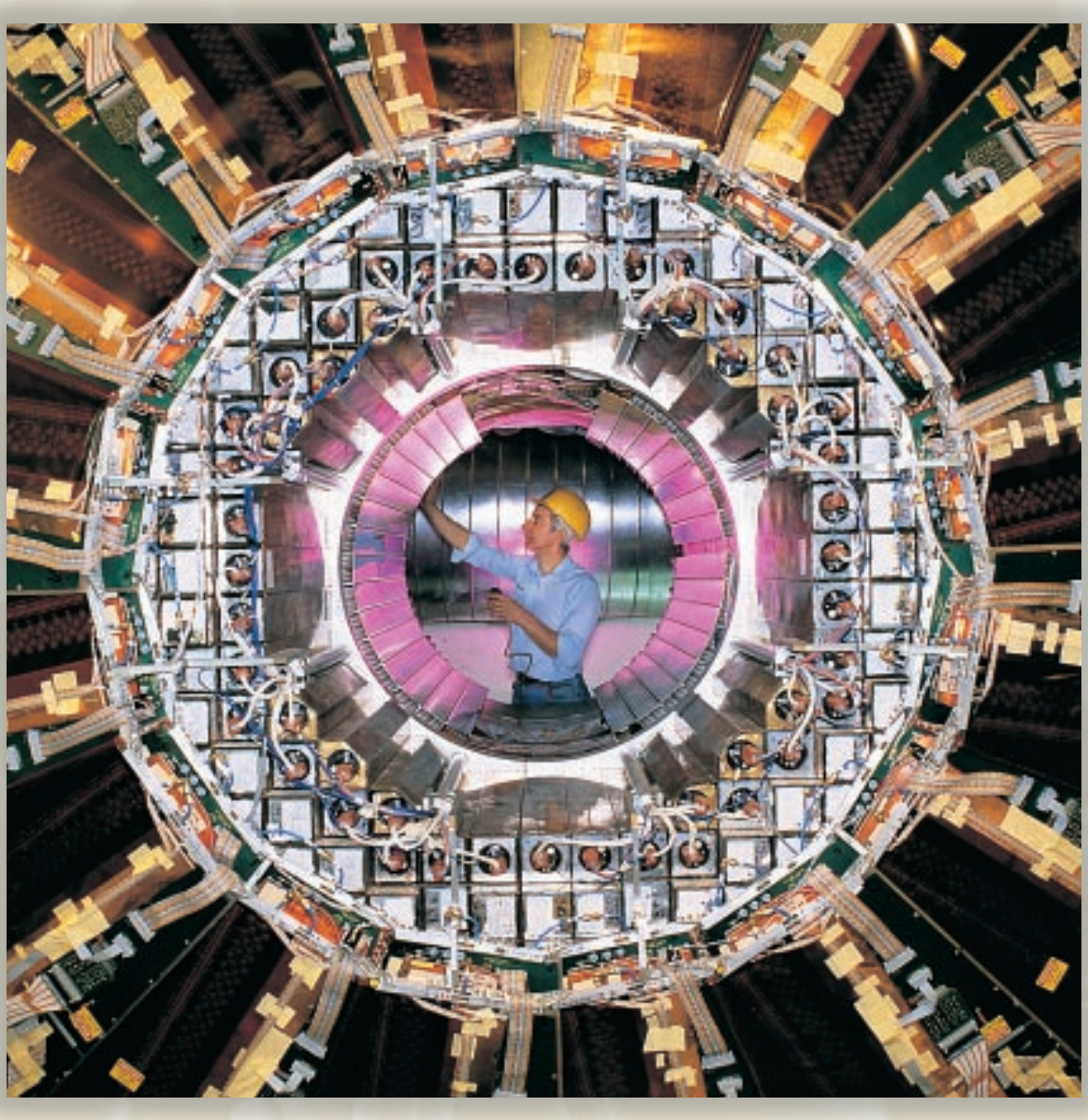
CHAPTER 22

Nuclear Chemistry



Particle detectors are important tools in the study of nuclear chemistry.

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The Nucleus

SECTION 22-1

Objectives

- Explain what a nuclide is, and describe the different ways nuclides can be represented.
- Define and relate the terms *mass defect* and *nuclear binding energy*.
- Explain the relationship between nucleon number and stability of nuclei.
- Explain why nuclear reactions occur, and know how to balance a nuclear equation.

Atomic nuclei are made of *protons and neutrons, which are collectively called* **nucleons.** In nuclear chemistry, *an atom is referred to as a* **nuclide** *and is identified by the number of protons and neutrons in its nucleus*. Nuclides can be represented in two ways: when a symbol such as $^{228}_{88}\text{Ra}$ is used, the superscript is the mass number and the subscript is the atomic number; the same nuclide can also be written as radium-228.

Mass Defect and Nuclear Stability

Because an atom is made of protons, neutrons, and electrons, you might expect the mass of an atom to be the same as the mass of an equal number of isolated protons, neutrons, and electrons. However, this is not the case. Let's consider a $^{4}_{2}\text{He}$ atom as an example. The combined mass of two protons, two neutrons, and two electrons is calculated below.

2 protons: $(2 \times 1.007\ 276\ \text{amu}) = 2.014\ 552\ \text{amu}$
2 neutrons: $(2 \times 1.008\ 665\ \text{amu}) = 2.017\ 330\ \text{amu}$
2 electrons: $(2 \times 0.000\ 5486\ \text{amu}) = \underline{0.001\ 097\ \text{amu}}$
total combined mass: $4.032\ 979\ \text{amu}$

However, the atomic mass of a $^{4}_{2}\text{He}$ atom has been measured to be 4.002 60 amu. The measured mass, 4.002 60 amu, is 0.030 38 amu *less* than the calculated mass, 4.032 98 amu. *The difference between the mass of an atom and the sum of the masses of its protons, neutrons, and electrons is called the* **mass defect.**

Nuclear Binding Energy

What causes the loss in mass? According to Albert Einstein's equation $E = mc^2$, mass can be converted to energy, and energy to mass. The mass defect is caused by the conversion of mass to energy upon formation of the nucleus. The mass units of the mass defect can be converted to energy units by using Einstein's equation. First, convert 0.030 38 amu to kilograms to match the units for energy, $\text{kg}\cdot\text{m}^2/\text{s}^2$.

$$0.030\ 38\ \text{amu} \times \frac{1.6605 \times 10^{-27}\ \text{kg}}{1\ \text{amu}} = 5.0446 \times 10^{-29}\ \text{kg}$$

CHEMISTRY INTERACTIVE TUTOR
Module 2: Models of the Atom

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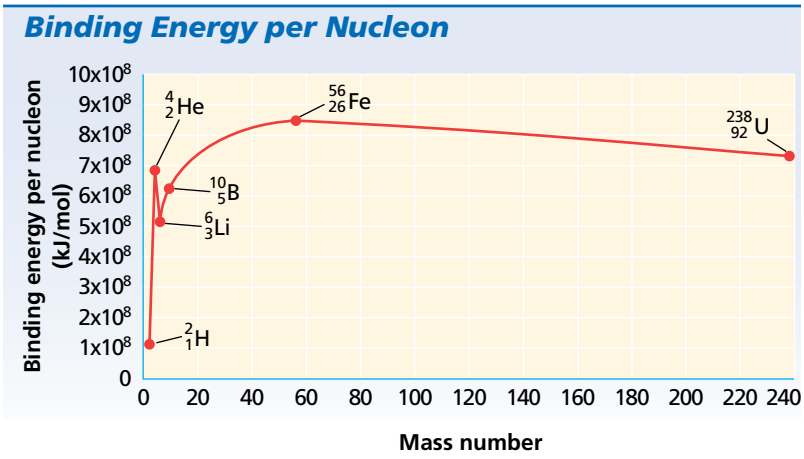

FIGURE 22-1 This graph shows the relationship between binding energy per nucleon and mass number. The binding energy per nucleon is a measure of the stability of a nucleus.

The energy equivalent can now be calculated.

$$E = mc^2$$
$$E = (5.0446 \times 10^{-29}\ \text{kg})(3.00 \times 10^{8}\ \text{m/s})^2$$
$$= 4.54 \times 10^{-12}\ \text{kg•m}^2/\text{s}^2 = 4.54 \times 10^{-12}\ \text{J}$$

This is the **nuclear binding energy,** *the energy released when a nucleus is formed from nucleons*. This energy can also be thought of as the amount of energy required to break apart the nucleus. Therefore, the nuclear binding energy is also a measure of the stability of a nucleus.

Binding Energy per Nucleon

The binding energy per nucleon is used to compare the stability of different nuclides, as shown in Figure 22-1. *The* **binding energy per nucleon** *is the binding energy of the nucleus divided by the number of nucleons it contains*. The higher the binding energy per nucleon, the more tightly the nucleons are held together. Elements with intermediate atomic masses have the greatest binding energies per nucleon and are therefore the most stable.

Nucleons and Nuclear Stability

Stable nuclides have certain characteristics. When the number of protons in stable nuclei is plotted against the number of neutrons, as shown in Figure 22-2, a beltlike graph is obtained. *This stable nuclei cluster over a range of neutron-proton ratios is referred to as the* **band of stability.** Among atoms having low atomic numbers, the most stable nuclei are those with a neutron-proton ratio of approximately 1:1. For example, $^{4}_{2}$He, a stable isotope of helium with two neutrons and two protons, has a neutron-proton ratio of 1:1. As the atomic number increases, the stable neutron-proton ratio increases to about 1.5:1. For example, $^{206}_{82}$Pb, with 124 neutrons and 82 protons, has a neutron-proton ratio of 1.51:1.

This trend can be explained by the relationship between the nuclear force and the electrostatic forces between protons. Protons in a nucleus repel all other protons through electrostatic repulsion, but the short

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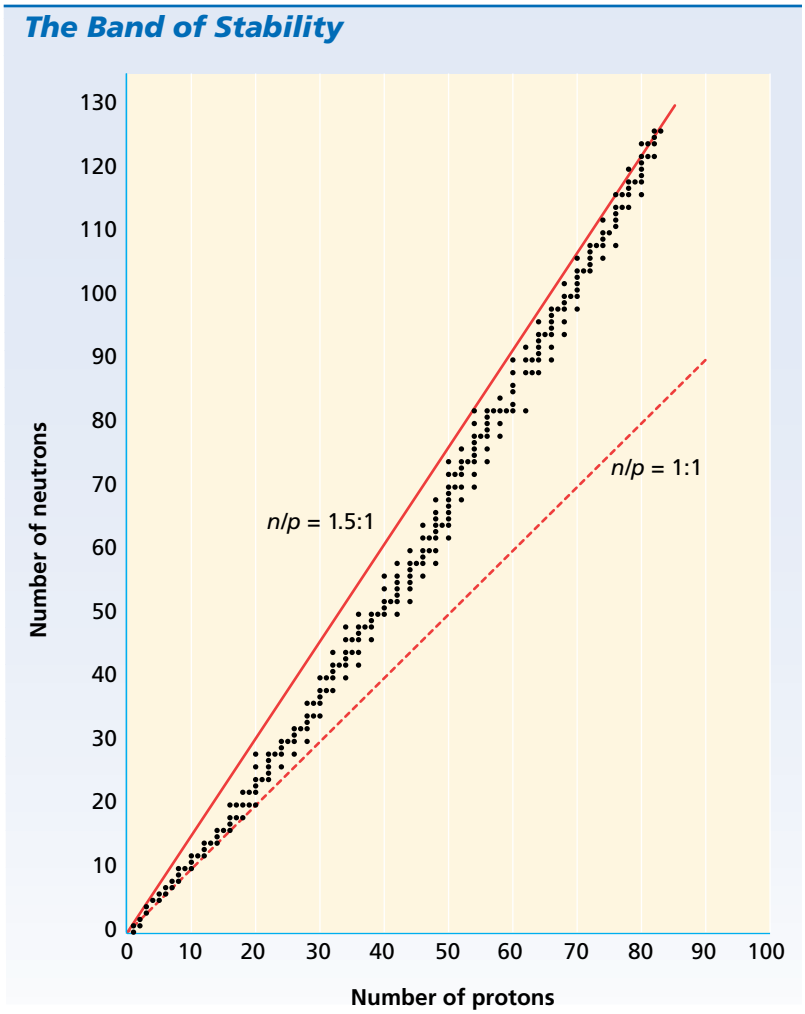

FIGURE 22-2 The neutron-proton ratios of stable nuclides cluster together in a region known as the band of stability. As the number of protons increases, the ratio increases from 1:1 to about 1.5:1.

range of the nuclear force allows them to attract only protons very close to them, as shown in Figure 22-3. So as the number of protons in a nucleus increases, the electrostatic force between protons increases faster than the nuclear force. More neutrons are required to increase the nuclear force and stabilize the nucleus. Beyond the atomic number 83, bismuth, the repulsive force of the protons is so great that no stable nuclides exist.

Stable nuclei tend to have even numbers of nucleons. Out of 265 stable nuclides, 159 have even numbers of both protons and neutrons. Only four nuclides have odd numbers of both. This indicates that stability of a nucleus is greatest when the nucleons—like electrons—are paired.

The most stable nuclides are those having 2, 8, 20, 28, 50, 82, or 126 protons, neutrons, or total nucleons. This extra stability at certain numbers supports a theory that nucleons—like electrons—exist at certain energy levels. According to the **nuclear shell model,** *nucleons exist in different energy levels, or shells, in the nucleus. The numbers of nucleons that represent completed nuclear energy levels—2, 8, 20, 28, 50, 82, and 126—are called* **magic numbers.**

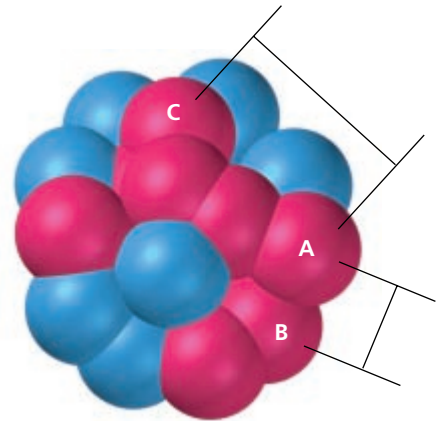

FIGURE 22-3 Proton A attracts proton B through the nuclear force but repels it through the electrostatic force. Proton A mainly repels proton C through the electrostatic force because the nuclear force reaches only a few nucleon diameters.

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Nuclear Reactions

Unstable nuclei undergo spontaneous changes that change their number of protons and neutrons. In this process, they give off large amounts of energy and increase their stability. These changes are a type of nuclear reaction. *A* **nuclear reaction** *is a reaction that affects the nucleus of an atom.* In equations representing nuclear reactions, the total of the atomic numbers and the total of the mass numbers must be equal on both sides of the equation. An example is shown below.

$$^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \longrightarrow ^{12}_{6}\text{C} + ^{1}_{0}n$$

Notice that when the atomic number changes, the identity of the element changes. *A* **transmutation** *is a change in the identity of a nucleus as a result of a change in the number of its protons.*

SAMPLE PROBLEM 22-1

Identify the product that balances the following nuclear reaction: $^{212}_{84}\text{Po} \longrightarrow ^{4}_{2}\text{He} + \underline{\ ?\ }$

SOLUTION

1. The total mass number and atomic number must be equal on both sides of the equation.

$$^{212}_{84}\text{Po} \longrightarrow ^{4}_{2}\text{He} + \underline{\ ?\ }$$

mass number: $212 - 4 = 208$

atomic number: $84 - 2 = 82$

2. The nuclide has a mass number of 208 and an atomic number of 82, $^{208}_{82}\text{Pb}$.

3. The balanced nuclear equation is $^{212}_{84}\text{Po} \longrightarrow ^{4}_{2}\text{He} + ^{208}_{82}\text{Pb}$

PRACTICE

Complete the following nuclear equations:

1. $^{218}_{84}\text{Po} \longrightarrow ^{4}_{2}\text{He} + \underline{\ ?\ }$ *Answer* $^{218}_{84}\text{Po} \longrightarrow ^{4}_{2}\text{He} + ^{214}_{82}\text{Pb}$
2. $^{253}_{99}\text{Es} + ^{4}_{2}\text{He} \longrightarrow ^{1}_{0}n + \underline{\ ?\ }$ *Answer* $^{253}_{99}\text{Es} + ^{4}_{2}\text{He} \longrightarrow ^{1}_{0}n + ^{256}_{101}\text{Md}$
3. $^{142}_{61}\text{Pm} + \underline{\ ?\ } \longrightarrow ^{142}_{60}\text{Nd}$ *Answer* $^{142}_{61}\text{Pm} + ^{0}_{-1}e \longrightarrow ^{142}_{60}\text{Nd}$

SECTION REVIEW

1. Define the following terms:
   a. nuclide
   b. nucleon
   c. mass defect
   d. nuclear binding energy
2. How is nuclear stability related to the neutron-proton ratio?
3. Why do unstable nuclides undergo nuclear reactions?
4. Complete and balance the following nuclear equations:
   a. $^{187}_{75}\text{Re} + \underline{\ ?\ } \longrightarrow ^{188}_{75}\text{Re} + ^{1}_{1}\text{H}$
   b. $^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \longrightarrow \underline{\ ?\ } + ^{1}_{0}n$
   c. $^{22}_{11}\text{Na} + \underline{\ ?\ } \longrightarrow ^{22}_{10}\text{Ne}$

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Radioactive Decay

SECTION 22-2

Objectives

- Define and relate the terms *radioactive decay* and *nuclear radiation.*
- Describe the different types of radioactive decay and their effects on the nucleus.
- Define the term *half-life*, and explain how it relates to the stability of a nucleus.
- Define and relate the terms *decay series, parent nuclide,* and *daughter nuclide.*
- Explain how artificial radioactive nuclides are made, and discuss their significance.

In 1896, Henri Becquerel was studying the possible connection between light emission of some uranium compounds after exposure to sunlight and X-ray emission. He wrapped a photographic plate in a lightproof covering and placed a uranium compound on top of it. He then placed them in sunlight. The photographic plate was exposed even though it was protected from visible light, suggesting exposure by X rays. When he tried to repeat his experiment, cloudy weather prevented him from placing the experiment in sunlight. To his surprise, the plate was still exposed. This meant that sunlight was not needed to produce the rays that exposed the plate. The rays were produced by radioactive decay. **Radioactive decay** *is the spontaneous disintegration of a nucleus into a slightly lighter nucleus, accompanied by emission of particles, electromagnetic radiation, or both.* The radiation that exposed the plate was **nuclear radiation,** *particles or electromagnetic radiation emitted from the nucleus during radioactive decay.*

Uranium is a **radioactive nuclide,** *an unstable nucleus that undergoes radioactive decay*. Studies by Marie Curie and Pierre Curie found that of the elements known in 1896, only uranium and thorium were radioactive. In 1898, the Curies discovered two new radioactive metallic elements, polonium and radium. Since that time, many other radioactive nuclides have been identified. In fact, all of the nuclides beyond atomic number 83 are unstable and thus radioactive.

Types of Radioactive Decay

A nuclide's type and rate of decay depend on the nucleon content and energy level of the nucleus. Some common types of radioactive nuclide emissions are summarized in Table 22-1.

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TABLE 22-1 *Radioactive Nuclide Emissions*

Type	Symbol	Charge	Mass (amu)
Alpha particle	$^{4}_{2}\mathrm{He}$	2+	4.002 60
Beta particle	$^{0}_{-1}\beta$	1−	0.000 5486
Positron	$^{0}_{+1}\beta$	1+	0.000 5486
Gamma ray	γ	0	0

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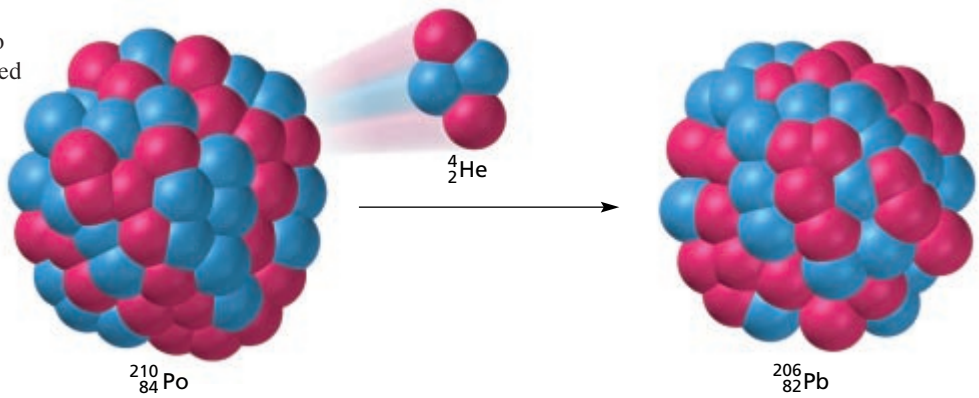

FIGURE 22-4 An alpha particle, identical to a helium nucleus, is emitted during the radioactive decay of some very heavy nuclei.

Alpha Emission

An **alpha particle** *(α) is two protons and two neutrons bound together and is emitted from the nucleus during some kinds of radioactive decay.* Alpha particles are helium nuclei and have a charge of 2+. They are often represented with the symbol $^{4}_{2}$He. Alpha emission is restricted almost entirely to very heavy nuclei. In these nuclei, both the number of neutrons and the number of protons need to be reduced in order to increase the stability of the nucleus. An example of alpha emission is the decay of $^{210}_{84}$Po into $^{206}_{82}$Pb, shown in Figure 22-4. The atomic number decreases by two, and the mass number decreases by four.

$$^{210}_{84}\text{Po} \longrightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

Beta Emission

Elements above the band of stability are unstable because they have too many neutrons. To decrease the number of neutrons, a neutron can be converted into a proton and an electron. The electron is emitted from the nucleus as a beta particle. *A* **beta particle** *(β) is an electron emitted from the nucleus during some kinds of radioactive decay.*

$$^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}\beta$$

An example of beta emission, shown in Figure 22-5, is the decay of $^{14}_{6}$C into $^{14}_{7}$N. Notice that the atomic number increases by one and the mass number stays the same.

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta$$

Positron Emission

Elements below the band of stability have too many protons to be stable. To decrease the number of protons, a proton can be converted into a neutron by emitting a positron. *A* **positron** *is a particle that has the same mass as an electron, but has a positive charge, and is emitted from the nucleus during some kinds of radioactive decay.*

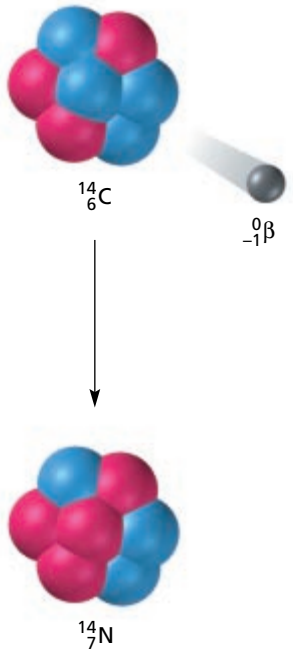

FIGURE 22-5 Beta emission causes the transmutation of $^{14}_{6}$C into $^{14}_{7}$N. Beta emission is a type of radioactive decay in which a proton is converted to a neutron with the emission of a beta particle.

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$$^{1}_{1}p \longrightarrow {}^{1}_{0}n + {}^{0}_{+1}\beta$$

An example of positron emission is the decay of $^{38}_{19}$K into $^{38}_{18}$Ar. Notice that the atomic number decreases by one but the mass number stays the same.

$$^{38}_{19}\text{K} \longrightarrow {}^{38}_{18}\text{Ar} + {}^{0}_{+1}\beta$$

Electron Capture

Another type of decay for nuclides with too many protons is electron capture. *In* **electron capture,** *an inner orbital electron is captured by the nucleus of its own atom.* The inner orbital electron combines with a proton, and a neutron is formed.

$$^{0}_{-1}e + {}^{1}_{1}p \longrightarrow {}^{1}_{0}n$$

An example of electron capture is the radioactive decay of $^{106}_{47}$Ag into $^{106}_{46}$Pd. Just as in positron emission, the atomic number decreases by one but the mass number stays the same.

$$^{106}_{47}\text{Ag} + {}^{0}_{-1}e \longrightarrow {}^{106}_{46}\text{Pd}$$

Gamma Emission

Gamma rays *(γ) are high-energy electromagnetic waves emitted from a nucleus as it changes from an excited state to a ground energy state.* The position of gamma rays in the electromagnetic spectrum is shown in Figure 22-6. The emission of gamma rays is another piece of evidence supporting the nuclear shell model. According to the nuclear shell model, gamma rays are produced when nuclear particles undergo transitions in nuclear-energy levels. This is similar to the emission of light when an electron drops to a lower-energy level, which was covered in Chapter 4. Gamma emission usually occurs immediately following other types of decay, when other types of decay leave the nucleus in an excited state.

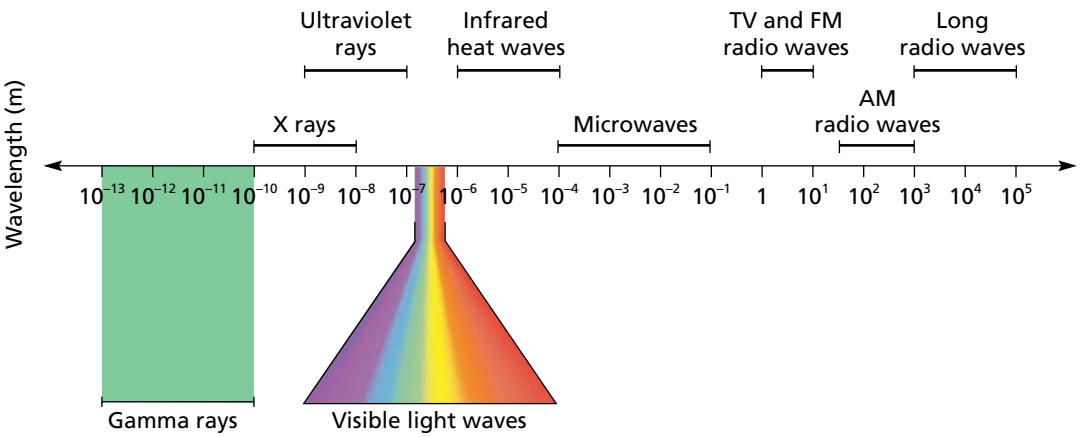
Ultraviolet rays
Infrared heat waves
TV and FM radio waves
Long radio waves
AM radio waves
X rays
Microwaves
Wavelength (m)
10^-13 10^-12 10^-11 10^-10 10^-9 10^-8 10^-7 10^-6 10^-5 10^-4 10^-3 10^-2 10^-1 1 10^1 10^2 10^3 10^4 10^5
Gamma rays
Visible light waves

FIGURE 22-6 Gamma rays, like visible light, are a form of electromagnetic radiation, but they have a much shorter wavelength and are much higher in energy than visible light.

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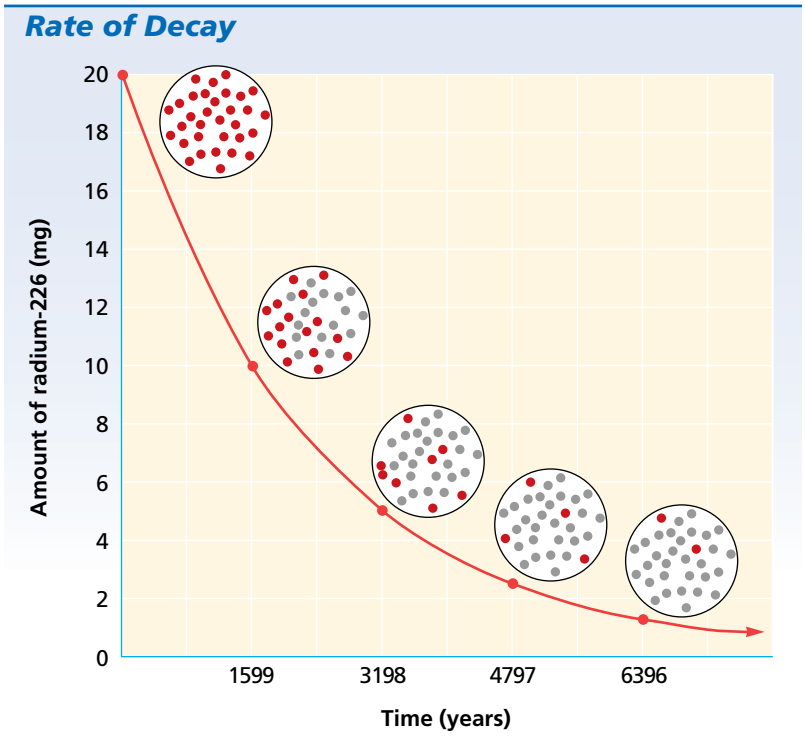

FIGURE 22-7 The half-life of radium-226 is 1599 years. Half of the remaining radium-226 decays by the end of each additional half-life.

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Half-Life

No two radioactive isotopes decay at the same rate. **Half-life,** $t_{1/2}$, *is the time required for half the atoms of a radioactive nuclide to decay.* Look at the graph of the decay of radium-226 in Figure 22-7. Radium-226 has a half-life of 1599 years. Half of a given amount of radium-226 decays in 1599 years. In another 1599 years, half of the remaining radium-226 decays. This process continues until there is a negligible amount of radium-226. Each radioactive nuclide has its own half-life. More-stable nuclides decay slowly and have longer half-lives. Less-stable nuclides decay very quickly and have shorter half-lives, sometimes just a fraction of a second. Some representative radioactive nuclides, along with their half-lives and types of decay, are given in Table 22-2.

TABLE 22-2 *Representative Radioactive Nuclides and Their Half-Lives*

Nuclide	Half-life	Nuclide	Half-life
$^{3}_{1}H$	12.32 years	$^{214}_{84}Po$	163.7 μs
$^{14}_{6}C$	5715 years	$^{218}_{84}Po$	3.0 min
$^{32}_{15}P$	14.28 days	$^{218}_{85}At$	1.6 s
$^{40}_{19}K$	1.3×10^{9} years	$^{238}_{92}U$	4.46×10^{9} years
$^{60}_{27}Co$	10.47 min	$^{239}_{94}Pu$	2.41×10^{4} years

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SAMPLE PROBLEM 22-2

Phosphorus-32 has a half-life of 14.3 days. How many milligrams of phosphorus-32 remain after 57.2 days if you start with 4.0 mg of the isotope?

SOLUTION

1 ANALYZE

Given: original mass of phosphorus-32 = 4.0 mg
half-life of phosphorus-32 = 14.3 days
time elapsed = 57.2 days

Unknown: mass of phosphorus-32 remaining after 57.2 days

2 PLAN

To determine the number of milligrams of phosphorus-32 remaining, we must first find the number of half-lives that have passed in the time elapsed. Then the amount of phosphorus-32 is determined by reducing the original amount by half for every half-life that has passed.

$$\text{number of half-lives} = \text{time elapsed (days)} \times \frac{1 \text{ half-life}}{14.3 \text{ days}}$$

$$\text{amount of phosphorus-32 remaining} = \text{original amount of phosphorus-32} \times \tfrac{1}{2} \text{ for each half-life}$$

3 COMPUTE

$$\text{number of half-lives} = 57.2 \cancel{\text{days}} \times \frac{1 \text{ half-life}}{14.3 \cancel{\text{days}}} = 4 \text{ half-lives}$$

$$\text{amount of phosphorus-32 remaining} = 4.0 \text{ mg} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} \times \tfrac{1}{2} = 0.25 \text{ mg}$$

4 EVALUATE

A period of 57.2 years is four half-lives for phosphorus-32. At the end of one half-life, 2.0 mg of phosphorus-32 remains; 1.0 mg remains at the end of two half-lives; 0.50 mg remains at the end of three half-lives; and 0.25 mg remains at the end of four half-lives.

PRACTICE

1. The half-life of polonium-210 is 138.4 days. How many milligrams of polonium-210 remain after 415.2 days if you start with 2.0 mg of the isotope?
   Answer 0.25 mg
2. Assuming a half-life of 1599 years, how many years will be needed for the decay of $\frac{15}{16}$ of a given amount of radium-226?
   Answer 6396 years
3. The half-life of radon-222 is 3.824 days. After what time will one-fourth of a given amount of radon remain?
   Answer 7.648 days
4. The half-life of cobalt-60 is 10.47 min. How many milligrams of cobalt-60 remain after 104.7 min if you start with 10.0 mg?
   Answer 0.00977 mg
5. A sample contains 4.0 mg of uranium-238. After 4.46×10^9 years, the sample will contain 2.0 mg of uranium-238. What is the half-life of uranium-238?
   Answer 4.46×10^9 years
6. A sample contains 16 mg of polonium-218. After 12 min, the sample will contain 1.0 mg of polonium-218. What is the half-life of polonium-218?
   Answer 3.0 min

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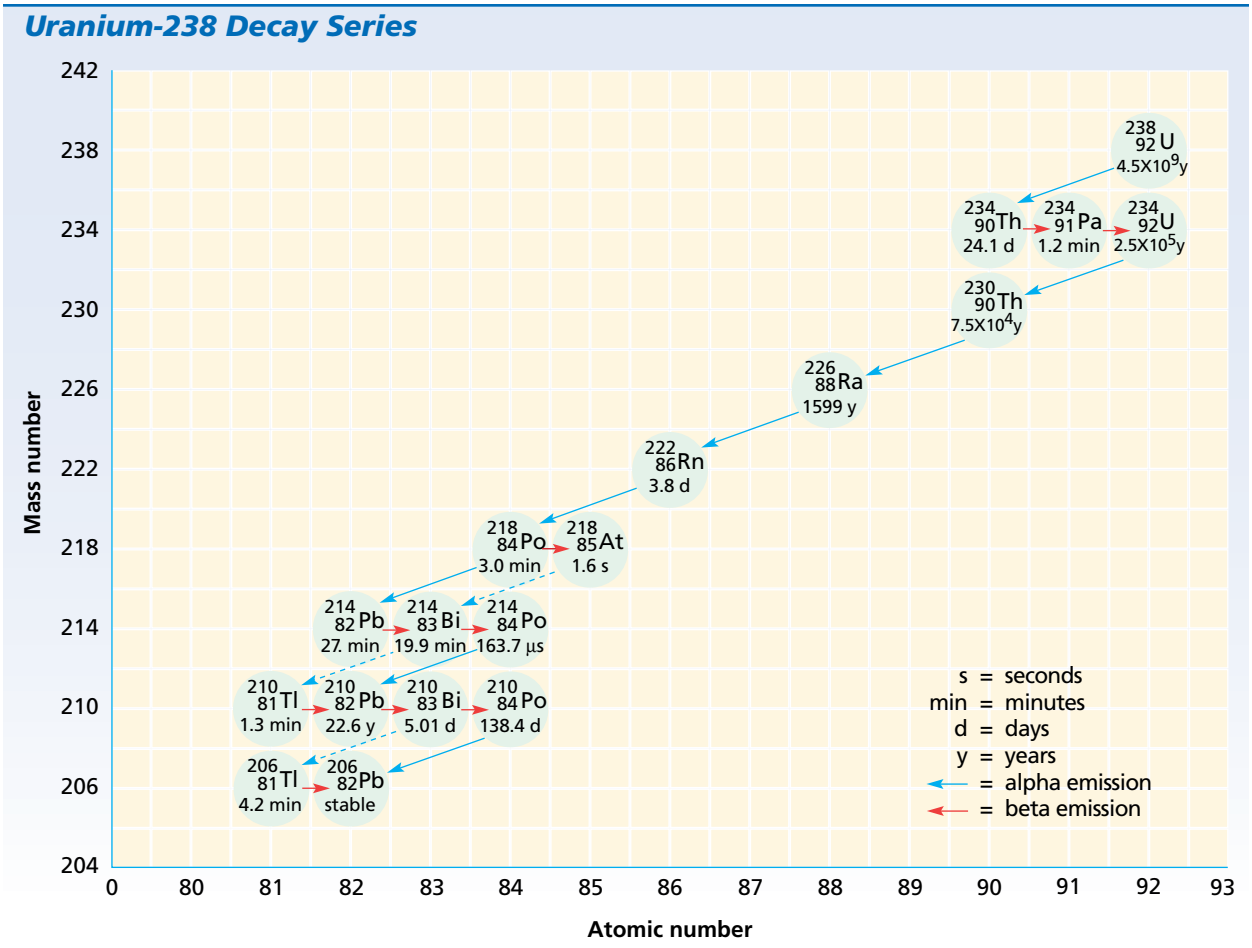
Decay Series

One nuclear reaction is not always enough to produce a stable nuclide. *A* **decay series** *is a series of radioactive nuclides produced by successive radioactive decay until a stable nuclide is reached. The heaviest nuclide of each decay series is called the* **parent nuclide.** *The nuclides produced by the decay of the parent nuclides are called* **daughter nuclides.** All naturally occurring nuclides with atomic numbers greater than 83 are radioactive and belong to one of three natural decay series. The parent nuclides are uranium-238, uranium-235, and thorium-232. The transmutations of the uranium-238 decay series are charted in Figure 22-8.

Locate the parent nuclide, uranium-238, on the chart. As the nucleus of uranium-238 decays, it emits an alpha particle. The mass number of the nuclide, and thus the vertical position on the graph, decreases by four. The atomic number, and thus the horizontal position, decreases by two. The daughter nuclide is an isotope of thorium.

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

FIGURE 22-8 This chart shows the transmutations that occur as $^{238}_{92}$U decays to the final, stable nuclide, $^{206}_{82}$Pb. Decay usually follows the solid arrows. The dotted arrows represent alternative routes of decay.



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The half-life of $^{234}_{90}Th$, about 24 days, is indicated on the chart. It decays by giving off beta particles. This increases its atomic number, and thus its horizontal position, by one. The mass number, and thus its vertical position, remains the same.

$$^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa + {}^{0}_{-1}\beta$$

The remaining atomic number and mass number changes shown on the decay chart are also explained in terms of the particles given off. In the final step, $^{210}_{84}Po$ loses an alpha particle to form $^{206}_{82}Pb$. This is a stable, nonradioactive isotope of lead. Notice that $^{206}_{82}Pb$ contains 82 protons, a magic number. It contains the extra-stable nuclear configuration of a completed nuclear shell.

Artificial Transmutations

Artificial radioactive nuclides are radioactive nuclides not found naturally on Earth. They are made by **artificial transmutations,** *bombardment of stable nuclei with charged and uncharged particles.* Because neutrons have no charge, they can easily penetrate the nucleus of an atom. However, positively charged alpha particles, protons, and other ions are repelled by the nucleus. Because of this repulsion, great quantities of energy are required to bombard nuclei with these particles. The necessary energy may be supplied by accelerating these particles in the magnetic or electrical field of a particle accelerator. An example of an accelerator is shown in Figure 22-9.

FIGURE 22-9 This is an aerial view of the Fermi International Accelerator Laboratory (Fermilab), in Illinois. The particle accelerators are underground. The Tevatron ring, the larger particle accelerator, has a circumference of 4 mi. The smaller ring in the background is a new accelerator, the Main Injector.

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TABLE 22-3 Reactions for the First Preparation of Several Transuranium Elements

Atomic number	Name	Symbol	Nuclear reaction
93	neptunium	Np	$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}\mathrm{U}$ $^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\beta$
94	plutonium	Pu	$^{238}_{93}\mathrm{Np} \longrightarrow {}^{238}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta$
95	americium	Am	$^{239}_{94}\mathrm{Pu} + 2\,{}^{1}_{0}n \longrightarrow {}^{241}_{95}\mathrm{Am} + {}^{0}_{-1}\beta$
96	curium	Cm	$^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}n$
97	berkelium	Bk	$^{241}_{95}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{243}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}n$
98	californium	Cf	$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{245}_{98}\mathrm{Cf} + {}^{1}_{0}n$
99	einsteinium	Es	$^{238}_{92}\mathrm{U} + 15\,{}^{1}_{0}n \longrightarrow {}^{253}_{99}\mathrm{Es} + 7\,{}^{0}_{-1}\beta$
100	fermium	Fm	$^{238}_{92}\mathrm{U} + 17\,{}^{1}_{0}n \longrightarrow {}^{255}_{100}\mathrm{Fm} + 8\,{}^{0}_{-1}\beta$
101	mendelevium	Md	$^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}n$
102	nobelium	No	$^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}n$
103	lawrencium	Lr	$^{252}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \longrightarrow {}^{258}_{103}\mathrm{Lr} + 4\,{}^{1}_{0}n$

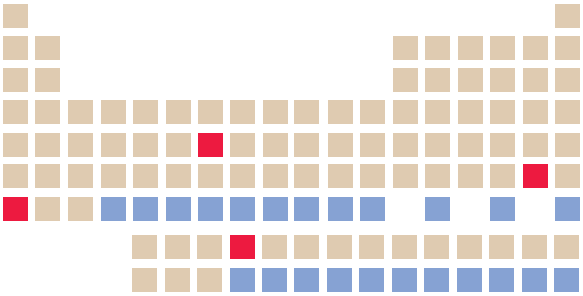

FIGURE 22-10 Artificial transmutations filled the gaps in the periodic table, shown in red, and extended the periodic table with the transuranium elements, shown in blue.

Artificial Radioactive Nuclides

Radioactive isotopes of all the natural elements have been produced by artificial transmutation. In addition, production of technetium, astatine, francium, and promethium by artificial transmutation has filled gaps in the periodic table. Their positions are shown in Figure 22-10.

Artificial transmutations are also used to produce the transuranium elements. **Transuranium elements** *are elements with more than 92 protons in their nuclei.* All of these elements are radioactive. The nuclear reactions for the synthesis of several transuranium elements are shown in Table 22-3. Currently, 17 artificially prepared transuranium elements have been reported. The positions of the transuranium elements in the periodic table are also shown in Figure 22-10.

SECTION REVIEW

1. Define *radioactive decay.*
2. a. What are the different types of radioactive decay?
   b. List the types of radioactive decay that involve conversion of particles.
3. What fraction of a given sample of a radioactive nuclide remains after four half-lives?
4. When does a decay series end?
5. Distinguish between natural and artificial radioactive nuclides.

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Nuclear Radiation

SECTION 22-3

OBJECTIVES

- Compare the penetrating ability and shielding requirements of alpha particles, beta particles, and gamma rays.
- Define the terms *roentgen* and *rem,* and distinguish between them.
- Describe three devices used in radiation detection.
- Discuss applications of radioactive nuclides.

In Becquerel's experiment, nuclear radiation from the uranium compound penetrated the lightproof covering and exposed the film. Different types of nuclear radiation have different penetrating abilities. Nuclear radiation includes alpha particles, beta particles, and gamma rays.

Alpha particles have a range of only a few centimeters in air and have a low penetrating ability due to their large mass and charge. They cannot penetrate skin. However, they can cause damage if ingested or inhaled. Beta particles travel at speeds close to the speed of light and have a penetrating ability about 100 times greater than that of alpha particles. They have a range of a few meters in air. Gamma rays have the greatest penetrating ability. The penetrating abilities and shielding requirements of different types of nuclear radiation are shown in Figure 22-11.

Radiation Exposure

Nuclear radiation can transfer its energy to the electrons of atoms or molecules and cause ionization. *The* **roentgen** *is a unit used to measure nuclear radiation; it is equal to the amount of radiation that produces* 2×10^9 *ion pairs when it passes through 1* cm^3 *of dry air.* Ionization can damage living tissue. Radiation damage to human tissue is measured in rems (roentgen equivalent, man). *One* **rem** *is the quantity of ionizing radiation that does as much damage to human tissue as is done by 1 roentgen of high-voltage X rays.* Cancer and genetic effects caused by DNA mutations are long-term radiation damage to living tissue. DNA

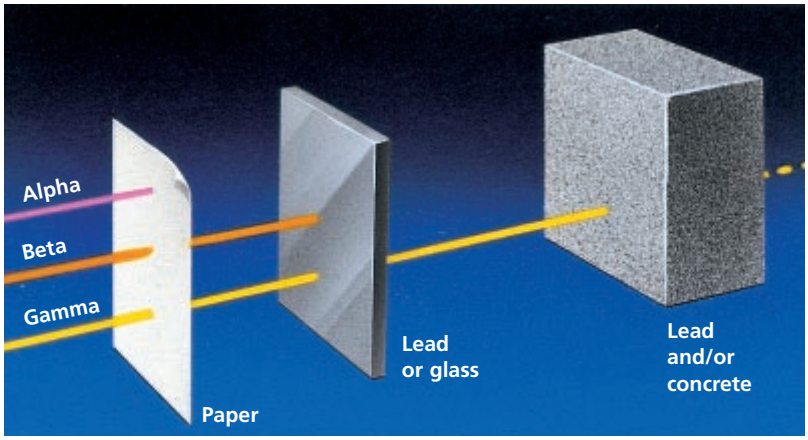

FIGURE 22-11 The different penetrating abilities of alpha particles, beta particles, and gamma rays require different levels of shielding. Alpha particles can be shielded with just a sheet of paper. Lead or glass is often used to shield beta particles. Gamma rays are the most penetrating and require shielding with thick layers of lead or concrete, or both.

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can be mutated directly by interaction with radiation or indirectly by interaction with previously ionized molecules.

Everyone is exposed to environmental background radiation. Average exposure for people living in the United States is estimated to be about 0.1 rem per year. However, actual exposure varies. The maximum permissible dose of radiation exposure for a person in the general population is 0.5 rem per year. Airline crews and people who live at high altitudes have increased exposure levels because of increased cosmic-ray levels at high altitudes. Radon-222 trapped inside homes may also cause increased exposure. Because it is a gas, radon can move up from the soil into homes through cracks and holes in the foundation. Radon trapped in homes increases the risk of lung cancer among smokers.

Radiation Detection

Film badges, Geiger-Müller counters, and scintillation counters are three devices commonly used to detect and measure nuclear radiation. A film badge and a Geiger-Müller counter are shown in Figure 22-12. As previously mentioned, nuclear radiation exposes film just as visible light does. This property is used in film badges. **Film badges** *use exposure of film to measure the approximate radiation exposure of people working with radiation.* **Geiger-Müller counters** *are instruments that detect radiation by counting electric pulses carried by gas ionized by radiation.* Geiger-Müller counters are typically used to detect beta-particle radiation. Radiation can also be detected when it transfers its energy to substances that *scintillate,* or absorb ionizing radiation and emit visible light. **Scintillation counters** *are instruments that convert scintillating light to an electric signal for detecting radiation.*

FIGURE 22-12 Film badges (a) and Geiger-Müller counters (b) are both used to detect nuclear radiation.

(a) (b)

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Applications of Nuclear Radiation

Many applications are based on the fact that the physical and chemical properties of stable isotopes are essentially the same as those of radioactive isotopes of the same element. A few uses of radioactive nuclides are discussed below.

Radioactive Dating

Radioactive dating *is the process by which the approximate age of an object is determined based on the amount of certain radioactive nuclides present.* Such an estimate is based on the fact that radioactive substances decay with known half-lives. Age is estimated by measuring either the accumulation of a daughter nuclide or the disappearance of the parent nuclide.

Carbon-14 is radioactive and has a half-life of approximately 5715 years. It can be used to estimate the age of organic material up to about 50 000 years old. Nuclides with longer half-lives are used to estimate the age of older objects; methods using nuclides with long half-lives have been used to date minerals and lunar rocks more than 4 billion years old.

Radioactive Nuclides in Medicine

In medicine, radioactive nuclides, such as the artificial radioactive nuclide cobalt-60, are used to destroy certain types of cancer cells. Many radioactive nuclides are also used as **radioactive tracers,** *which are radioactive atoms that are incorporated into substances so that movement of the substances can be followed by radiation detectors.* Detection of radiation from radioactive tracers can be used to diagnose cancer and other diseases. See Figure 22-13.

Radioactive Nuclides in Agriculture

In agriculture, radioactive tracers in fertilizers are used to determine the effectiveness of the fertilizer. The amount of radioactive tracer absorbed by a plant indicates the amount of fertilizer absorbed. Nuclear radiation is also used to prolong the shelf life of food. For example, gamma rays from cobalt-60 can be used to kill bacteria and insects that spoil and infest food.

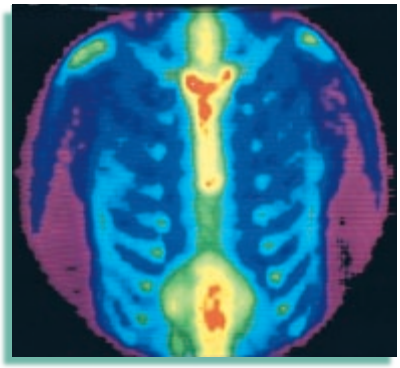

FIGURE 22-13 Radioactive nuclides, such as technetium-99, can be used to detect bone cancer. In this procedure, technetium-99 accumulates in areas of abnormal bone metabolism. Detection of the nuclear radiation then shows the location of bone cancer.

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Nuclear Waste

Nuclear Fission and Nuclear Fusion

In nuclear fission, the nucleus of a very heavy atom, such as uranium, is split into two or more nuclei. The products of the fission include the nuclei as well as the nuclides formed from the fragments' radioactive decay. Fission is the primary system powering nuclear reactors, nuclear missiles, and nuclear-powered submarines and aircraft carriers. Fusion is the opposite process of fission. In fusion, very high temperatures and pressures are used to combine light atoms, such as hydrogen, to make heavier atoms, such as helium. Fusion is the primary process that fuels

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our sun and the stars. Creating and maintaining a fusion reaction is more complex and expensive than performing fission. Both fission and fusion release enormous amounts of energy that can be converted into heat and electricity, and both produce **nuclear waste.** Fission produces more waste than fusion. As new processes are developed to use energy from fission and fusion, a more vexing question arises: how to contain, store, and dispose of nuclear waste.

Containment of Nuclear Waste

Every radioactive substance has a half-life, which is the amount of time needed for half of a given material to decay into a stable nuclear form and lose its radioactivity. Radioactive waste from medical research, for example, has a half-life of a few months. Waste that is produced in a nuclear reactor will take hundreds of thousands of years to decay, and it needs to be contained so that living organisms can be shielded from radioactivity. There are two main types of containment: on-site storage and off-site disposal.

Storage of Nuclear Waste

The most common form of nuclear waste is spent fuel rods from nuclear power plants. These fuel rods can be contained above the ground by placing them in water pools or in dry casks. Each nuclear reactor in the United States has large pools of water where spent rods can be stored, and some of the radioactive materials will decay. When these pools are full, the rods are moved to dry casks, which are usually made of concrete and steel. Both storage pools and casks are meant for only temporary storage before the waste is moved to permanent underground storage facilities.

Disposal of Nuclear Waste

Disposal of nuclear waste is done with the intention of never retrieving the materials. Because of this, building disposal sites takes careful planning. Currently, there are 77 disposal sites around the United States. The U. S. Department of Energy is considering a new site near Las Vegas, Nevada, called Yucca Mountain, for the permanent disposal of much of this waste. This plan, however, is controversial—some organizations oppose the idea of the disposal site, and others have alternate plans. If the Yucca Mountain site is approved, nuclear waste will be transported there by truck and train beginning in 2010.

SECTION REVIEW

1. What is required to shield alpha particles? Why are these materials effective?
2. a. What is the average exposure of people living in the United States to environmental background radiation?
   b. How does this relate to the maximum permissible dose?
3. What device is used to measure the radiation exposure of people working with radiation?
4. Explain why nuclear radiation can be used to preserve food.
5. Explain how nuclear waste is contained, stored, and disposed of, and how each method affects the environment.

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Nuclear Fission and Nuclear Fusion

SECTION 22-4

Objectives

- Define *nuclear fission, chain reaction,* and *nuclear fusion,* and distinguish between them.
- Explain how a fission reaction is used to generate power.
- Discuss the possible benefits and the current difficulty of controlling fusion reactions.

Nuclear Fission

Review Figure 22-1 on page 702, which shows that nuclei of intermediate mass are the most stable. *In* **nuclear fission,** *a very heavy nucleus splits into more-stable nuclei of intermediate mass.* This process releases enormous amounts of energy. Nuclear fission can occur spontaneously or when nuclei are bombarded by particles. When uranium-235 is bombarded with slow neutrons, a uranium nucleus may capture one of the neutrons, making it very unstable. The nucleus splits into medium-mass parts with the emission of more neutrons. The mass of the products is less than the mass of the reactants. The missing mass is converted to energy.

Nuclear Chain Reaction

When fission of an atom bombarded by neutrons produces more neutrons, a chain reaction can occur. *A* **chain reaction** *is a reaction in which the material that starts the reaction is also one of the products and can start another reaction.* As shown in Figure 22-14, two or three neutrons can be given off when uranium-235 fission occurs. These neutrons can cause the fission of other uranium-235 nuclei. Again neutrons are emitted, which

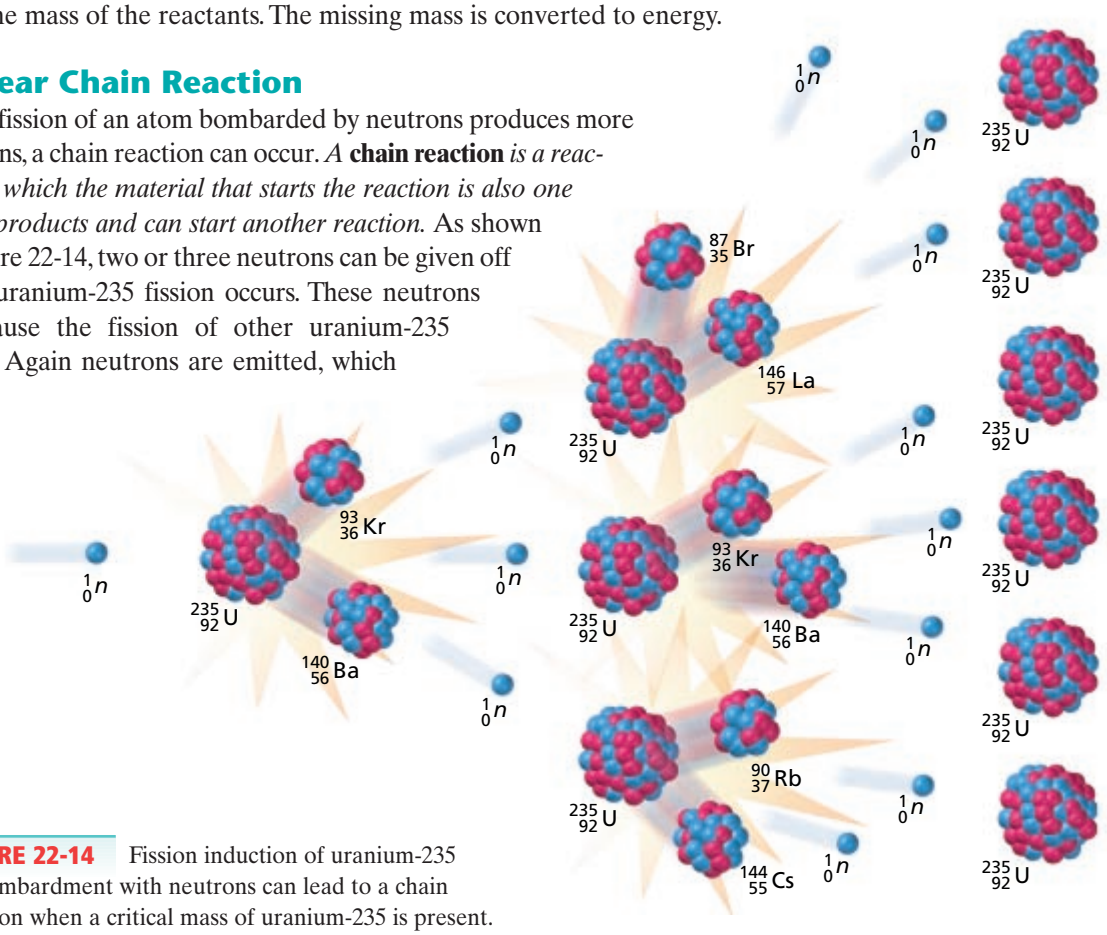

FIGURE 22-14 Fission induction of uranium-235 by bombardment with neutrons can lead to a chain reaction when a critical mass of uranium-235 is present.

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can cause the fission of still other uranium-235 nuclei. This chain reaction continues until all of the uranium-235 atoms have split or until the neutrons fail to strike uranium-235 nuclei. If the mass of uranium-235 is below a certain minimum, too many neutrons will escape without striking other nuclei, and the chain reaction will stop. *The minimum amount of nuclide that provides the number of neutrons needed to sustain a chain reaction is called the* **critical mass.** Uncontrolled chain reactions provide the explosive energy of atomic bombs. **Nuclear reactors** *use controlled-fission chain reactions to produce energy or radioactive nuclides*.

Nuclear Power Plants

Nuclear power plants *use heat from nuclear reactors to produce electrical energy*. They have five main components: shielding, fuel, control rods, moderator, and coolant. The components, shown in Figure 22-15, are surrounded by shielding. **Shielding** *is radiation-absorbing material that is used to decrease exposure to radiation, especially gamma rays, from nuclear reactors*. Uranium-235 is typically used as the fissionable fuel to produce heat, which is absorbed by the coolant. **Control rods** *are neutron-absorbing rods that help control the reaction by limiting the number of free neutrons.* Because fission of uranium-235 is more efficiently induced by slow neutrons, a **moderator** *is used to slow down the fast neutrons produced by fission*. Current problems with nuclear power plant development include environmental requirements, safety of operation, plant construction costs, and storage and disposal of spent fuel and radioactive wastes.

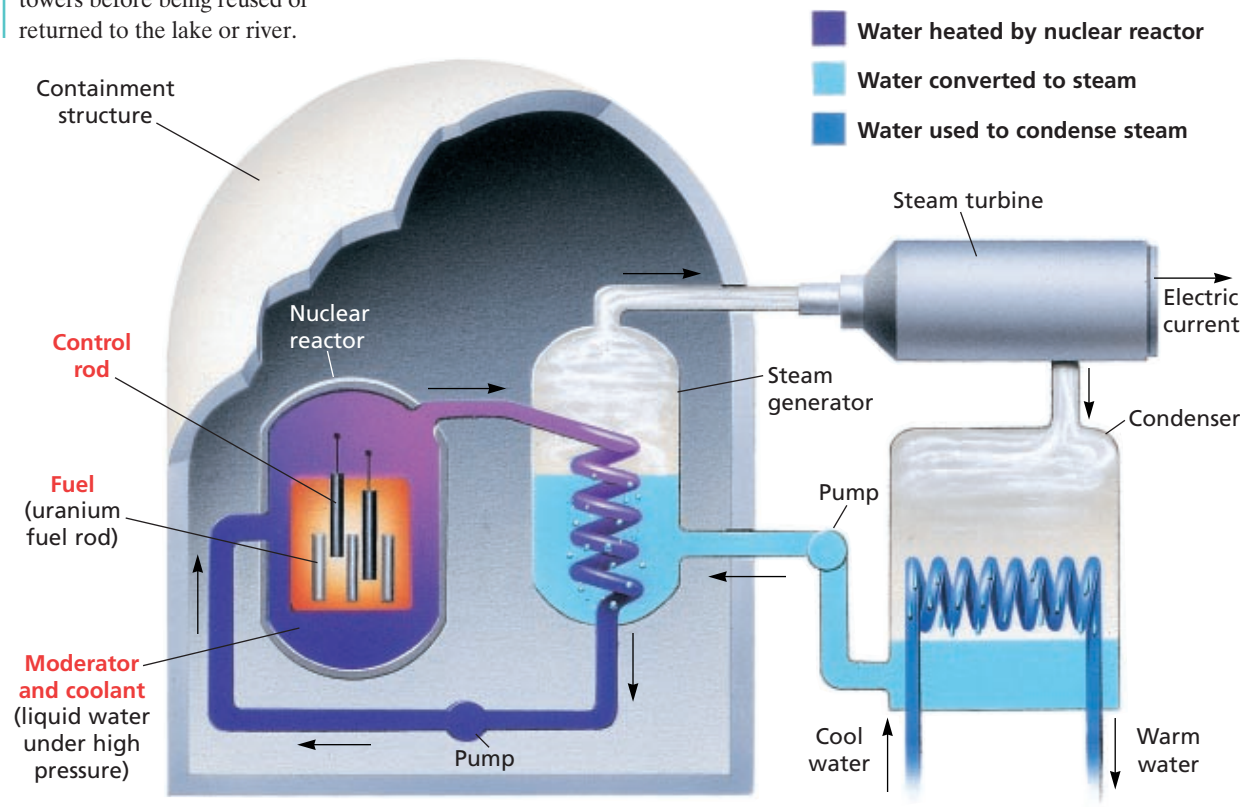

FIGURE 22-15 In this model of a nuclear power plant, pressurized water is heated by fission of uranium-235. This water is circulated to a steam generator. The steam drives a turbine to produce electricity. Cool water from a lake or river is then used to condense the steam into water. The warm water from the condenser may be cooled in cooling towers before being reused or returned to the lake or river.

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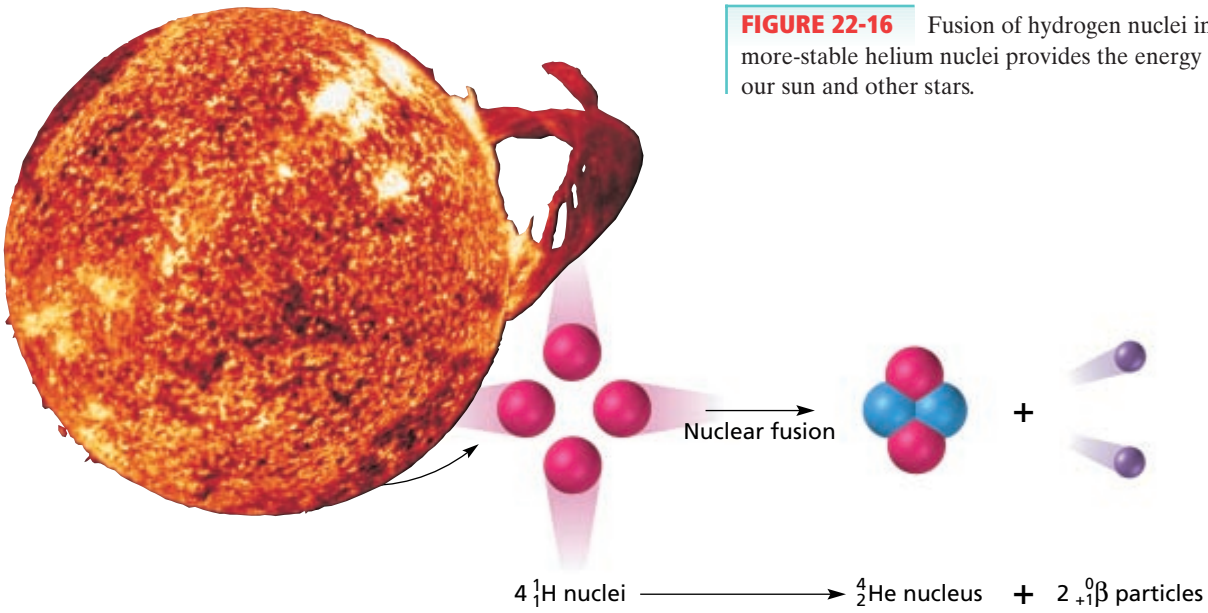

FIGURE 22-16 Fusion of hydrogen nuclei into more-stable helium nuclei provides the energy of our sun and other stars.

Nuclear Fusion

The high stability of nuclei with intermediate masses can also be used to explain nuclear fusion. *In* **nuclear fusion,** *light-mass nuclei combine to form a heavier, more stable nucleus.* Nuclear fusion releases even more energy per gram of fuel than nuclear fission. In our sun and other stars, four hydrogen nuclei combine at extremely high temperature and pressure to form a helium nucleus with a loss of mass and release of energy. This reaction is illustrated in Figure 22-16.

Uncontrolled fusion reactions of hydrogen are the source of energy for the hydrogen bomb, as shown in Figure 22-17. A fission reaction is used to provide the heat and pressure necessary to trigger the fusion of nuclei. Current research indicates that fusion reactions may be controllable if some major problems can be overcome. One of the problems is that no known material can withstand the initial temperatures, about 10^8 K, required to induce fusion at high temperatures. Methods that contain the fusion reactions within a magnetic field or induce fusion at lower temperatures are being investigated.

FIGURE 22-17 The enormous amount of energy released by fusion reactions is illustrated by this explosion of a hydrogen bomb.

SECTION REVIEW

1. Distinguish between nuclear fission and nuclear fusion.
2. Define *chain reaction.*
3. List the five main components of a nuclear power plant.
4. Explain how fusion is one of our sources of energy.

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An Unexpected Finding

HISTORICAL PERSPECTIVE

The discovery of the artificial transmutation of uranium in 1934 triggered great excitement in science. Chemists preoccupied with identifying what they thought were the final missing elements of the periodic table suddenly had to consider the existence of elements beyond atomic number 92, while physicists began to probe the stability of the nucleus more deeply. By 1939, nuclear investigators in both fields had collaborated to provide a stunning explanation for the mysterious results of uranium's forced transformation.

Neutrons in Italy

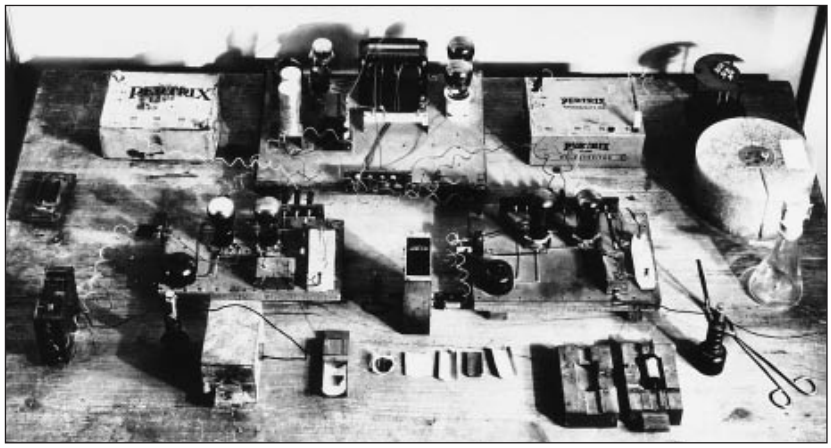
In 1934, uranium had the most protons of any known element, 92. But that year, Italian physicist Enrico Fermi believed he had synthesized elements with even higher atomic numbers. After bombarding a sample of uranium with neutrons, Fermi and co-workers recorded measurements that seemed to indicate that some uranium nuclei had absorbed neutrons and then undergone beta decay:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}? + {}^{0}_{-1}\beta$$

His report noted further, subsequent beta decays, by which he hypothesized the existence of a whole new series of "transuranic" elements:

$$^{238}_{92}\mathrm{U} \longrightarrow {}^{238}_{93}? + {}^{0}_{-1}\beta \longrightarrow {}^{238}_{94}?? + {}^{0}_{-1}\beta \longrightarrow {}^{238}_{95}??? + {}^{0}_{-1}\beta$$

Unfortunately, the Italian group could not verify the existence of the transuranes because, as Fermi put it, "We did not know enough chemistry to separate the products of uranium disintegration from one another."



This apparatus from Otto Hahn's lab was used to produce fission reactions.

Curiosity in Berlin

Fermi's experiments caught the attention of a physicist in Berlin, Lise Meitner. Knowing that she could not perform the difficult task of chemically separating radionuclides either, Meitner persuaded a colleague, radiochemist Otto Hahn, to help her explain Fermi's results. Joined by expert chemical analyst Fritz Strassman, the team began investigating neutron-induced uranium decay at the end of 1934.

From the onset, the Berlin team, along with all other scientists at the time, operated under two false assumptions. The first involved the makeup of the bombarded nuclei. In every nuclear reaction observed previously, the resulting nucleus had never differed from the original by more than a few protons or neutrons. Thus, it was assumed that the products of neutron bombardment were radioisotopes of elements at most a few places in the periodic table before or beyond the atoms being bombarded (as Fermi had presumed in hypothesizing the transuranes).

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The second assumption concerned the periodicity of the transuranes. Because the elements Ac, Th, Pa, and U chemically resembled the third-row transition elements, La, Hf, Ta, and W, it was believed that elements beyond U would correspondingly resemble those following W. Thus, the transuranes were thought to be homologues of Re, Os, Ir, Pt, and so on. This belief was generally unquestioned and seemed to be confirmed. In fact, by 1937 Hahn was sure of the chemical evidence of transuranes:

> *. . . the chemical behavior of the transuranes . . . is such that their position in the periodic system is no longer in doubt. . . . their chemical distinction from all previously known elements needs no further discussion.*

Meitner's Exile

By 1938, the political situation in Germany had become dangerous for Meitner. Because she was of Jewish descent, she was being targeted by the Nazis and fled to Sweden to escape persecution. Meanwhile in Berlin, the anti-Nazi Hahn and Strassman had to be careful of every move they made under the watchful eyes of the fascists around them.

Despite censorship, the Berlin team continued to communicate through letters. Meitner could not come up with a satisfying physical explanation for the chemical results of Hahn and Strassman, and she insisted that her partners re-examine their findings. As Strassman later recalled, Meitner

> *. . . requested that [the] experiments be scrutinized . . . one more time. . . . Fortunately L. Meitner's opinion and judgment carried so much weight . . . the necessary control experiments were immediately undertaken.*

The politics of World War II prevented Lise Meitner from receiving the Nobel Prize in physics for explaining nuclear fission.

A Shocking Discovery

Prompted by Meitner, Hahn and Strassman realized they had been looking in the wrong place to find the cause of their results. In analyzing a fraction of a solution assay that they had previously ignored, they found the critical evidence they had been seeking.

The analysis indicated that barium appeared to be a result of neutron bombardment of uranium. Suspecting the spectacular truth but lacking confidence, Hahn wrote to Meitner for an explanation. After consultation with her nephew, Otto Frisch, Meitner proposed that the uranium nuclei had been broken apart into elemental fragments, one of which was Ba. On January 3, 1939, she wrote to Hahn:

> *. . . the two of you really do have a splitting to Ba . . . a truly beautiful result, for which I most heartily congratulate you and Strassman.*

Thus, the transuranes turned out to be merely radioisotopes of known elements—atomic fragments of uranium atoms that had burst apart on being struck by neutrons.

For the discovery of this unexpected phenomenon, which Meitner named nuclear fission, the talented Hahn was awarded the 1944 Nobel Prize in chemistry. Due to wartime politics, however, Lise Meitner did not receive the corresponding award in physics, and she was not popularly recognized until well after her death in 1968 for her role in clarifying the process that she first explained and named.

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CHAPTER 22 REVIEW

CHAPTER SUMMARY

22-1

- The difference between the sum of the masses of the nucleons and electrons in an atom and the actual mass of an atom is the mass defect, or nuclear binding energy.
- Nuclear stability tends to be greatest when nucleons are paired, when there are magic numbers of nucleons, and when there are certain neutron-proton ratios.
- Nuclear reactions, represented by nuclear equations, can involve the transmutation of nuclides.

Vocabulary

band of stability (702)
binding energy per nucleon (702)
magic numbers (703)
mass defect (701)
nuclear binding energy (702)
nuclear reaction (704)
nuclear shell model (703)
nucleons (701)
nuclide (701)
transmutation (704)

22-2

- Radioactive nuclides become more stable by radioactive decay, a type of nuclear reaction.
- Alpha, beta, positron, and gamma emission, and electron capture are all types of radioactive decay. A nuclide's type of decay is related to its nucleon content and the energy level of the nucleus.
- The half-life of a radioactive nuclide is the length of time that it takes for half of a given number of atoms of the nuclide to decay.
- A decay series starts with a parent nuclide and ends with a stable daughter nuclide.
- Artificial transmutations are used to produce artificial radioactive nuclides, including the transuranium elements.

Vocabulary

alpha particle (706)
artificial transmutations (711)
beta particle (706)
daughter nuclides (710)
decay series (710)
electron capture (707)
gamma ray (707)
half-life (708)
nuclear radiation (705)
parent nuclide (710)
positron (706)
radioactive decay (705)
radioactive nuclide (705)
transuranium elements (712)

22-3

- Alpha particles, beta particles, and gamma rays have different penetrating abilities and therefore different shielding requirements.
- Film badges, Geiger-Müller counters, and scintillation detectors are used to detect radiation.
- Everyone is exposed to environmental background radiation. Exposure levels vary.
- Radioactive nuclides have many uses, including radioactive dating and cancer detection.
- Nuclear waste must be contained, stored, and disposed of in a way that does not harm people or the environment.

Vocabulary

film badges (714)
Geiger-Müller counters (714)
nuclear waste (716)
radioactive dating (715)
radioactive tracers (715)
rem (713)
roentgen (713)
scintillation counters (714)

22-4

- Nuclear fission and nuclear fusion are nuclear reactions in which the splitting and fusing of nuclei produce more stable nuclei and release enormous amounts of energy.
- Controlled fission reactions are used to produce energy and radioactive nuclides.
- Fusion reactions produce the sun's heat and light. If fusion reactions could be controlled, they would produce more usable energy per gram of fuel than fission reactions.

Vocabulary

chain reaction (717)
control rods (718)
critical mass (718)
moderator (718)
nuclear fission (717)
nuclear fusion (719)
nuclear power plant (718)
nuclear reactors (718)
shielding (718)

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REVIEWING CONCEPTS

1. a. How does mass defect relate to nuclear binding energy?
   b. How does binding energy per nucleon vary with mass number?
   c. How does binding energy per nucleon affect the stability of a nucleus? (22-1)
2. Describe three ways in which the number of protons and the number of neutrons in a nucleus affect its stability. (22-1)
3. Where on the periodic table are most of the natural radioactive nuclides located? (22-2)
4. What changes in atomic number and mass number occur in each of the following types of radioactive decay?
   a. alpha emission
   b. beta emission
   c. positron emission
   d. electron capture (22-2)
5. Which types of radioactive decay cause the transmutation of a nuclide? (Hint: Review the definition of *transmutation.*) (22-2)
6. Explain how beta emission, positron emission, and electron capture affect the neutron-proton ratio. (22-2)
7. Write out the nuclear reactions that show particle conversion for the following types of radioactive decay:
   a. beta emission
   b. positron emission
   c. electron capture (22-2)
8. Compare and contrast electrons, beta particles, and positrons. (22-2)
9. a. What are gamma rays?
   b. How do scientists think they are produced? (22-2)
10. How does the half-life of a nuclide relate to its stability? (22-2)
11. List the three parent nuclides of the natural decay series. (22-2)
12. How are artificial radioactive isotopes produced? (22-2)
13. Neutrons are more effective than protons or alpha particles for bombarding atomic nuclei. Why? (22-2)
14. Why are all of the transuranium elements radioactive? (Hint: See Section 22-1.) (22-2)
15. Why can a radioactive material affect photographic film even though the film is well wrapped in black paper? (22-3)
16. How does the penetrating ability of gamma rays compare with that of alpha particles and beta particles? (22-3)
17. How does nuclear radiation damage biological tissue? (22-3)
18. Explain how film badges, Geiger-Müller counters, and scintillation detectors are used to detect radiation and measure radiation exposure. (22-3)
19. How is the age of an object containing a radioactive nuclide estimated? (22-3)
20. How is the fission of a uranium-235 nucleus induced? (22-4)
21. How does the fission of uranium-235 produce a chain reaction? (22-4)
22. Describe the purposes of the five major components of a nuclear power plant. (22-4)
23. Describe the reaction that produces the sun's energy. (22-4)
24. What is one problem that must be overcome before energy-producing controlled fusion reactions are a reality? (22-4)

PROBLEMS

Mass Defect

25. The mass of a $^{20}_{10}$Ne atom is 19.992 44 amu. Calculate its mass defect.
26. The mass of a $^{7}_{3}$Li atom is 7.016 00 amu. Calculate its mass defect.

Nuclear Binding Energy

27. Calculate the nuclear binding energy of one lithium-6 atom. The measured atomic mass of lithium-6 is 6.015 amu.
28. Calculate the binding energies of the following two nuclei, and indicate which releases more

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energy when formed. You will need information from the periodic table and the text.

a. atomic mass 34.988011 amu, $^{35}_{19}K$

b. atomic mass 22.989767 amu, $^{23}_{11}Na$

29. a. What is the binding energy per nucleon for each nucleus in the previous problem?

b. Which nucleus is more stable?

30. The mass of $^{7}_{3}Li$ is 7.016 00 amu. Calculate the binding energy per nucleon for $^{7}_{3}Li$. Convert the mass in amu to binding energy in joules.

Neutron-Proton Ratio

31. Calculate the neutron-proton ratios for the following nuclides:

a. $^{12}_{6}C$ c. $^{206}_{82}Pb$

b. $^{3}_{1}H$ d. $^{134}_{50}Sn$

32. a. Locate the nuclides in problem 31 on the graph in Figure 22-2. Which ones lie on the band of stability?

b. For the stable nuclides, determine whether their neutron-proton ratio tends toward 1:1 or 1.5:1.

Nuclear Equations

33. Balance the following nuclear equations. (Hint: See Sample Problem 22-1.)

a. $^{43}_{19}K \longrightarrow {}^{43}_{20}Ca + \underline{\ ?\ }$

b. $^{233}_{92}U \longrightarrow {}^{229}_{90}Th + \underline{\ ?\ }$

c. $^{11}_{6}C + \underline{\ ?\ } \longrightarrow {}^{11}_{5}B$

d. $^{13}_{7}N \longrightarrow {}^{0}_{+1}\beta + \underline{\ ?\ }$

34. Write the nuclear equation for the release of an alpha particle by $^{210}_{84}Po$.

35. Write the nuclear equation for the release of a beta particle by $^{210}_{82}Pb$.

Half-Life

36. The half-life of plutonium-239 is 24 110 years. Of an original mass of 100.g, how much remains after 96 440 years? (Hint: See Sample Problem 22-2.)

37. The half-life of thorium-227 is 18.72 days. How many days are required for three-fourths of a given amount to decay?

38. Exactly $\frac{1}{16}$ of a given amount of protactinium-234 remains after 26.76 hours. What is the half-life of protactinium-234?

39. How many milligrams remain of a 15.0 mg sample of radium-226 after 6396 years? The half-life of radium-226 is 1599 years.

MIXED REVIEW

40. Balance the following nuclear reactions;

a. $^{239}_{93}Np \longrightarrow {}^{0}_{-1}\beta + \underline{\ ?\ }$

b. $^{9}_{4}Be + {}^{4}_{2}He \longrightarrow \underline{\ ?\ }$

c. $^{32}_{15}P + \underline{\ ?\ } \longrightarrow {}^{33}_{15}P$

d. $^{236}_{92}U \longrightarrow {}^{94}_{36}Kr + \underline{\ ?\ } + 3{}^{1}_{0}n$

41. After 4797 years, how much of an original 0.250 g of radium-226 remains? Its half-life is 1599 years.

42. The parent nuclide of the thorium decay series is $^{232}_{90}Th$. The first four decays are as follows: alpha emission, beta emission, beta emission, and alpha emission. Write the nuclear equations for this series of emissions.

43. The half-life of radium-224 is 3.66 days. What was the original mass of radium-224 if 0.0500 g remains after 7.32 days?

44. Calculate the neutron-proton ratios for the following nuclides, and determine where they lie in relation to the band of stability.

a. $^{235}_{92}U$ c. $^{56}_{26}Fe$

b. $^{16}_{8}O$ d. $^{156}_{60}Nd$

45. Calculate the binding energy per nucleon of $^{238}_{92}U$ in joules. The atomic mass of a $^{238}_{92}U$ nucleus is 238.050 784 amu.

46. The energy released by the formation of a nucleus of $^{56}_{26}Fe$ is 7.89×10^{-11} J. Use Einstein's equation, $E = mc^2$, to determine how much mass is lost (in kilograms) in this process.

47. Calculate the binding energy for one mole of deuterium atoms. The measured mass of deuterium is 2.0140 amu.

CRITICAL THINKING

48. Why do we compare binding energy per nuclear particle of different nuclides instead of the total binding energy per nucleus?

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49. Why is the constant rate of decay of radioactive nuclei so important in radioactive dating?

50. Which of the following nuclides of carbon is most likely to be stable? State reasons for your answer.
a. $^{11}_{6}C$ b. $^{12}_{6}C$

51. Which of the following nuclides of iron are most likely to be stable? State reasons for your answer.
a. $^{56}_{26}Fe$ b. $^{59}_{26}Fe$

52. Use the data in the table shown to determine
a. which isotopes would be best for dating ancient rocks.
b. which isotopes could be used as tracers.
State reasons for your answers.

Element	Half-Life
Potassium-40	1.28×10^9 yr
Potassium-42	12.36 h
Uranium-238	4.468×10^9 yr
Uranium-239	23.47 min

RESEARCH & WRITING

53. Investigate the history of the Manhattan Project.

54. Research the 1986 nuclear reactor accident at Chernobyl, Ukraine. What factors combined to cause the accident?

55. Find out about the various fusion-energy research projects that are being conducted in the United States and other parts of the world. How close are the researchers to finding an economical method of producing energy? What obstacles must still be overcome?

ALTERNATIVE ASSESSMENT

56. Using the library, research the medical uses of radioactive isotopes such as cobalt-60 and technetium-99. Evaluate the benefits and risks of using radioisotopes in the diagnosis and treatment of medical conditions. Report your findings to the class.

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Back

GLOSSARY

A

absolute zero the temperature –273.15°C, given a value of zero in the Kelvin scale (317)

accuracy the closeness of measurements to the correct or accepted value of the quantity measured (44)

acid-base indicator a compound whose color is sensitive to pH (493)

acid-ionization constant the term K_a (569)

actinide one of the 14 elements with atomic numbers from 90 (thorium, Th) through 103 (lawrencium, Lr) (126)

activated complex a transitional structure that results from an effective collision and that persists while old bonds are breaking and new bonds are forming (535)

activation energy the minimum energy required to transform the reactants into an activated complex (534)

activity series a list of elements organized according to the ease with which the elements undergo certain chemical reactions (265)

actual yield the measured amount of a product obtained from a reaction (293)

addition polymer a polymer formed by chain addition reactions between monomers that contain a double bond (686)

addition reaction a reaction in which an atom or molecule is added to an unsaturated molecule and increases the saturation of the molecule (682)

alcohol an organic compound that contains one or more hydroxyl groups (663)

aldehyde an organic compound in which a carbonyl group is attached to a carbon atom at the end of a carbon-atom chain (672)

alkali metal one of the elements of Group 1 of the periodic table (lithium, sodium, potassium, rubidium, cesium, and francium) (132)

alkaline a solution in which a base has completely dissociated in water to yield aqueous OH^- ions (461)

alkaline-earth metal one of the elements of Group 2 of the periodic table (beryllium, magnesium, calcium, strontium, barium, and radium) (132)

alkane a hydrocarbon that contains only single bonds (634)

alkene a hydrocarbon that contains double covalent bonds (647)

alkyl group a group of atoms that is formed when one hydrogen atom is removed from an alkane molecule (637)

alkyl halide an organic compound in which one or more halogen atoms —fluorine, chlorine, bromine, or iodine—are substituted for one or more hydrogen atoms in a hydrocarbon (666)

alkyne a hydrocarbon with triple covalent bonds (651)

alpha particle two protons and two neutrons bound together and emitted from the nucleus during some kinds of radioactive decay (706)

amine an organic compound that can be considered to be a derivative of ammonia, NH_3 (677)

amorphous solid a solid in which the particles are arranged randomly (368)

amphoteric any species that can react as either an acid or a base (471)

angular momentum quantum number the quantum number that indicates the shape of the orbital (101)

anion a negative ion (149)

anode the electrode where oxidation takes place (607)

aromatic hydrocarbon a hydrocarbon with six-membered carbon rings and delocalized electrons (652)

Arrhenius acid a chemical compound that increases the concentration of hydrogen ions, H^+, in aqueous solution (459)

Arrhenius base a substance that increases the concentration of hydroxide ions, OH^-, in aqueous solution (459)

artificial transmutation bombardment of stable nuclei with charged and uncharged particles (711)

atmosphere of pressure exactly equivalent to 760 mm Hg (311)

atom the smallest unit of an element that maintains the properties of that element (10)

atomic mass unit a unit of mass that is exactly 1/12 the mass of a carbon-12 atom, or $1.660\,540 \times 10^{-27}$ kg (78)

atomic number the number of protons in the nucleus of each atom of an element (75)

atomic radius one-half the distance between the nuclei of identical atoms that are bonded together (140)

Aufbau principle an electron occupies the lowest-energy orbital that can receive it (105)

autooxidation a process in which a substance acts as both an oxidizing agent and a reducing agent (605)

average atomic mass the weighted average of the atomic masses of the naturally occurring isotopes of an element (79)

Avogadro's law equal volumes of gases at the same temperature and pressure contain equal numbers of molecules (334)

Avogadro's number $6.022\,1367 \times 10^{23}$; the number of particles in exactly one mole of a pure substance (81)

B

band of stability the stable nuclei cluster over a range of neutron-proton ratios (702)

barometer a device used to measure atmospheric pressure (310)

benzene the primary aromatic hydrocarbon (652)

beta particle an electron emitted from the nucleus during some kinds of radioactive decay (706)

binary acid an acid that contains only two different elements: hydrogen and one of the more-electronegative elements (454)

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binary compound a compound composed of two different elements (206)

binding energy per nucleon the binding energy of the nucleus divided by the number of nucleons it contains (702)

boiling the conversion of a liquid to a vapor within the liquid as well as at its surface; occurs when the equilibrium vapor pressure of the liquid equals the atmospheric pressure (378)

boiling point the temperature at which the equilibrium vapor pressure of a liquid equals the atmospheric pressure (378)

boiling-point elevation the difference between the boiling point of a pure solvent and a nonelectrolyte of that solvent, directly proportional to the molal concentration of the solution (440)

bond energy the energy required to break a chemical bond and form neutral isolated atoms (167)

bond length the distance between two bonded atoms at their minimum potential energy, that is, the average distance between two bonded atoms (167)

Boyle's law the volume of a fixed mass of gas varies inversely with pressure at constant temperature (314)

Brønsted-Lowry acid a molecule or ion that is a proton donor (464)

Brønsted-Lowry acid-base reaction the transfer of protons from one reactant (the acid) to another (the base) (465)

Brønsted-Lowry base a molecule or ion that is a proton acceptor (465)

buffered solution a solution that can resist changes in pH (570)

C

calorimeter a device used to measure the heat absorbed or released in a chemical or physical change (511)

capillary action the attraction of the surface of a liquid to the surface of a solid (365)

carboxylic acid an organic compound that contains the carboxyl functional group (674)

catalysis the action of a catalyst (540)

catalyst a substance that changes the rate of a chemical reaction without itself being permanently consumed (540)

catenation the covalent binding of an element to itself to form chains or rings (630)

cathode the electrode where reduction takes place (607)

cation a positive ion (149)

chain reaction a reaction in which the material that starts the reaction is also one of the products and can start another reaction (717)

change of state a physical change of a substance from one state to another (12)

Charles's law the volume of a fixed mass of gas at constant pressure varies directly with the Kelvin temperature (317)

chemical any substance that has a definite composition (6)

chemical bond a mutual electrical attraction between the nuclei and valence electrons of different atoms that binds the atoms together(161)

chemical change a change in which one or more substances are converted into different substances (13)

chemical equation a representation, with symbols and formulas, of the identities and relative amounts of the reactants and products in a chemical reaction (241)

chemical equilibrium a state of balance in which the rate of a forward reaction equals the rate of its reverse reaction and the concentrations of its products and reactants remain unchanged (554)

chemical-equilibrium expression the equation for the equilibrium constant, K (556)

chemical formula a formula that indicates the relative numbers of atoms of each kind in a chemical compound by using atomic symbols and numerical subscripts (164)

chemical kinetics the area of chemistry that is concerned with reaction rates and reaction mechanisms (538)

chemical property the ability of a substance to undergo a change that transforms it into a different substance (12)

chemical reaction a reaction in which one or more substances are converted into different substances (13)

chemistry the study of the composition, structure, and properties of matter and the changes it undergoes (5)

coefficient a small whole number that appears in front of a formula in a chemical equation (243)

colligative properties properties that depend on the concentration of solute particles but not on their identity (436)

collision theory the set of assumptions regarding collisions and reactions (532)

colloid a mixture consisting of particles that are intermediate in size between those in solutions and suspensions forming mixtures known as colloid dispersions (397)

combined gas law the relationship between the pressure, volume, and temperature of a fixed amount of gas (321)

combustion reaction a reaction in which a substance combines with oxygen, releasing a large amount of energy in the form of light and heat (263)

common ion effect the phenomenon in which the addition of an ion common to two solutes brings about precipitation or reduced ionization (567)

composition reaction a reaction in which two or more substances combine to form a new compound (256)

composition stoichiometry calculations involving the mass relationships of elements in compounds (275)

compound a substance that is made from the atoms of two or more elements that are chemically bonded (11)

concentration a measure of the amount of solute in a given amount of solvent or solution (412)

condensation the process by which a gas changes to a liquid (373)

condensation polymer a polymer formed by condensation reactions (690)

condensation reaction a reaction in which two molecules or parts of the same molecule combine (683)

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conjugate acid the species that is formed when a Brønsted-Lowry base gains a proton (469)

conjugate base the species that remains after a Brønsted-Lowry acid has given up a proton (469)

continuous spectrum the emission of a continuous range of frequencies of electromagnetic radiation (94)

control rod a neutron-absorbing rod that helps control a nuclear reaction by limiting the number of free neutrons (718)

conversion factor a ratio derived from the equality between two different units that can be used to convert from one unit to the other (40)

copolymer a polymer made from two different monomers (685)

covalent bonding a chemical bond resulting from the sharing of an electron pair between two atoms (161)

critical mass the minimum amount of nuclide that provides the number of neutrons needed to sustain a chain reaction (718)

critical point indicates the critical temperature and critical pressure of a substance (381)

critical pressure the lowest pressure at which a substance can exist as a liquid at the critical temperature (382)

critical temperature the temperature above which a substance cannot exist in the liquid state (381)

crystal a substance in which the particles are arranged in an orderly, geometric, repeating pattern (368)

crystal structure the total three-dimensional arrangement of particles of a crystal (369)

crystalline solid a solid consisting of crystals (368)

cycloalkane an alkane in which the carbon atoms are arranged in a ring, or cyclic, structure (635)

D

Dalton's law of partial pressures the total pressure of a mixture of gases is equal to the sum of the partial pressures of the component gases (322)

daughter nuclide a nuclide produced by the decay of a parent nuclide (710)

decay series a series of radioactive nuclides produced by successive radioactive decay until a stable nuclide is reached (710)

decomposition reaction a reaction in which a single compound produces two or more simpler substances (259)

delocalized electron an electron shared by more than two atoms (627)

density the ratio of mass to volume or mass divided by volume (38)

deposition the change of state from a gas directly to a solid (380)

derived unit a unit that is a combination of SI base units (36)

diamond a colorless, crystalline, solid form of carbon (626)

diatomic molecule a molecule containing only two atoms (164)

diffusion spontaneous mixing of the particles of two substances caused by their random motion (305)

dipole equal but opposite charges that are separated by a short distance (190)

dipole-dipole force a force of attraction between polar molecules (190)

diprotic acid an acid that can donate two protons per molecule (466)

direct proportion two quantities that give a constant value when one is divided by the other (55)

displacement reaction a reaction in which one element replaces a similar element in a compound (261)

dissociation the separation of ions that occurs when an ionic compound dissolves (425)

double bond a covalent bond produced by the sharing of two pairs of electrons between two atoms (172)

double-replacement reaction a reaction in which the ions of two compounds exchange places in an aqueous solution to form two new compounds (262)

ductility the ability of a substance to be drawn, pulled, or extruded through a small opening to produce a wire (182)

E

effervescence the rapid escape of a gas from the liquid in which it is dissolved (407)

effusion a process by which gas particles pass through a tiny opening (306)

elastic collision a collision between gas particles and between gas particles and container walls in which there is no net loss of kinetic energy (303)

electrochemical cell a system of electrodes and electrolytes in which either chemical reactions produce electrical energy or an electric current produces chemical change (607)

electrochemistry the branch of chemistry that deals with electricity-related applications of oxidation-reduction reactions (606)

electrode a conductor used to establish electrical contact with a nonmetallic part of a circuit, such as an electrolyte (607)

electrode potential the difference in potential between an electrode and its solution (613)

electrolysis the process in which an electric current is used to produce an oxidation-reduction reaction (610); also the decomposition of a substance by an electric current (259)

electrolyte a substance that dissolves in water to give a solution that conducts electric current (399)

electrolytic cell an electrochemical cell in which electrical energy is required to produce a redox reaction and bring about a chemical change (610)

electromagnetic radiation a form of energy that exhibits wavelike behavior as it travels through space (91)

electromagnetic spectrum all the forms of electromagnetic radiation (91)

electron affinity the energy change that occurs when an electron is acquired by a neutral atom (147)

electron capture the process in which an inner orbital electron is captured by the nucleus of its own atom (707)

electron configuration the arrangement of electrons in an atom (105)

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electron-dot notation an electron-configuration notation in which only the valence electrons of an atom of a particular element are shown, indicated by dots placed around the element's symbol (170)

electronegativity a measure of the ability of an atom in a chemical compound to attract electrons (151)

electroplating an electrolytic process in which a metal ion is reduced and solid metal is deposited on a surface (611)

element a pure substance made of only one kind of atom (10)

elimination reaction a reaction in which a simple molecule, such as water or ammonia, is removed from adjacent carbon atoms of a larger molecule (684)

empirical formula the symbols for the elements combined in a compound with subscripts showing the smallest whole-number mole ratio of the different atoms in the compound (229)

end point the point in a titration at which an indicator changes color (498)

enthalpy change the amount of energy absorbed or lost by a system during a process at constant pressure (516)

entropy a measure of the degree of randomness of the particles, such as molecules, in a system (527)

equilibrium a dynamic condition in which two opposing changes occur at equal rates in a closed system (372)

equilibrium constant the ratio of the mathematical product of the concentrations of substances formed at equilibrium to the mathematical product of the concentrations of the reacting substances. Each concentration is raised to a power equal to the coefficient of that substance in the chemical equation (556)

equilibrium vapor pressure the pressure exerted by a vapor in equilibrium with its corresponding liquid at a given temperature (376)

equivalence point the point at which the two solutions used in a titration are present in chemically equivalent amounts (498)

ester an organic compound with a carboxylic acid group in which the hydrogen of the hydroxyl group has been replaced by an alkyl group (675)

ether an organic compound in which two hydrocarbon groups are bonded to the same atom of oxygen (669)

evaporation the process by which particles escape from the surface of a nonboiling liquid and enter the gas state (365)

excess reactant the substance that is not used up completely in a reaction (288)

excited state a state in which an atom has a higher potential energy than it has in its ground state (94)

extensive property a property that depends on the amount of matter that is present (11)

F

family a vertical column of the periodic table (21)

film badge a device that uses exposure of film to measure the approximate radiation exposure of people working with radiation (714)

fluid a substance that can flow and therefore take the shape of its container; a liquid or a gas (305)

formula equation a representation of the reactants and products of a chemical reaction by their symbols or formulas (244)

formula mass the sum of the average atomic masses of all the atoms represented in the formula of any molecule, formula unit, or ion (221)

formula unit the simplest collection of atoms from which an ionic compound's formula can be established (176)

fractional distillation distillation in which components of a mixture are separated, on the basis of boiling point, by condensation of vapor in a fractionating column (644)

free energy the combined enthalpy-entropy function of a system (528)

free-energy change the difference between the change in enthalpy, ΔH, and the product of the Kelvin temperature and the entropy change, which is defined as $T\Delta S$, at a constant pressure and temperature (528)

freezing the physical change of a liquid to a solid by the removal of heat (366)

freezing point the temperature at which a solid and liquid are in equilibrium at 1 atm (101.3 kPa) pressure (379)

freezing-point depression the difference between the freezing points of a pure solvent and a solution of a nonelectrolyte in that solvent; is directly proportional to the molal concentration of the solution (438)

frequency the number of waves that pass a given point in a specific time, usually one second (91)

fullerene a dark-colored solid made of spherically networked carbon-atom cages (626)

functional group an atom or group of atoms that is responsible for the specific properties of an organic compound (663)

G

gamma ray a high-energy electromagnetic wave emitted from a nucleus as it changes from an excited state to a ground energy state (707)

gas the state of matter in which a substance has neither definite volume nor definite shape (12)

gas laws simple mathematical relationships between the volume, temperature, pressure, and quantity of a gas (313)

Gay-Lussac's law the pressure of a fixed mass of gas at constant volume varies directly with the Kelvin temperature (319)

Gay-Lussac's law of combining volumes of gases at constant temperature and pressure, the volumes of gaseous reactants and products can be expressed as ratios of small whole numbers (333)

Geiger-Müller counter an instrument that detects radiation by counting electric pulses carried by gas ionized by radiation (714)

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geometric isomers isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different (632)

Graham's law of effusion the rates of effusion of gases at the same temperature and pressure are inversely proportional to the square roots of their molar masses (352)

graphite a soft, black, crystalline form of carbon that is a fair conductor of electricity (626)

ground state the lowest energy state of an atom (94)

group a vertical column of the periodic table (21)

H

half-cell a single electrode immersed in a solution of its ions (607)

half-life the time required for half the atoms of a radioactive nuclide to decay (708)

half-reaction the part of a reaction involving oxidation or reduction alone (593)

halogen one of the elements of Group 17 (fluorine, chlorine, bromine, iodine, and astatine) (137)

heat the energy transferred between samples of matter because of a difference in their temperature (512)

heat of combustion energy released as heat by the complete combustion of one mole of a substance (519)

heat of reaction the quantity of energy released or absorbed as heat during a chemical reaction (514)

heat of solution the net amount of energy absorbed or released as heat when a specific amount of solute dissolves in a solvent (410)

Heisenberg uncertainty principle it is impossible to determine simultaneously both the position and velocity of an electron or any other particle (99)

Henry's law the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas on the surface of the liquid (407)

Hess's law the overall enthalpy change in a reaction is equal to the sum of the enthalpy changes for the individual steps in the process (519)

heterogeneous not having a uniform composition throughout (16)

heterogeneous catalyst a catalyst whose phase is different from that of the reactants (540)

heterogeneous reaction a reaction involving reactants in two different phases (538)

highest occupied energy level the electron-containing main energy level with the highest principal quantum number (110)

homogeneous having a uniform composition throughout (16)

homogeneous catalyst a catalyst that is in the same phase as all the reactants and products in a reaction system (540)

homogeneous reaction a reaction whose reactants and products exist in a single phase (532)

homologous series a series in which adjacent members differ by a constant unit (634)

Hund's rule orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin (106)

hybrid orbitals orbitals of equal energy produced by the combination of two or more orbitals on the same atom (188)

hybridization the mixing of two or more atomic orbitals of similar energies on the same atom to produce new orbitals of equal energies (187)

hydration a solution process with water as the solvent (405)

hydrocarbon the simplest organic compound, composed of only carbon and hydrogen (630)

hydrogen bonding the intermolecular force in which a hydrogen atom that is bonded to a highly electronegative atom is attracted to an unshared pair of electrons of an electronegative atom in a nearby molecule (192)

hydrolysis a reaction between water molecules and ions of a dissolved salt (572)

hydronium ion the H_3O^+ ion (431)

hypothesis a testable statement (30)

I

ideal gas an imaginary gas that perfectly fits all the assumptions of the kinetic-molecular theory (303)

ideal gas constant the constant R, 0.082 057 84 L·atm/mol·K(342)

ideal gas law the mathematical relationship of pressure, volume, temperature, and the number of moles of a gas (340)

immiscible liquid solutes and solvents that are not soluble in each other (406)

inner-shell electron an electron that is not in the highest occupied energy level (110)

intensive property a property that does not depend on the amount of matter present (11)

intermediate a species that appears in some steps of a reaction but not in the net equation (532)

intermolecular force the force of attraction between molecules (189)

inverse proportion two quantities that have a constant mathematical product (56)

ion an atom or group of bonded atoms that has a positive or negative charge (143)

ionic bonding the chemical bond resulting from electrical attraction between large numbers of cations and anions (161)

ionic compound a compound composed of positive and negative ions that are combined so that the numbers of positive and negative charges are equal (176)

ionization the formation of ions from solute molecules by the action of the solvent (431); any process that results in the formation of an ion (143)

ionization energy the energy required to remove one electron from a neutral atom of an element (143)

isomers compounds that have the same molecular formula but different structures (630)

isotopes atoms of the same element that have different masses (76)

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J

joule the SI unit of heat energy as well as all other forms of energy (511)

K

ketone an organic compound in which a carbonyl group is attached to a carbon atom within the chain (672)

kinetic-molecular theory a theory based on the idea that particles of matter are always in motion (303)

L

lanthanide one of the 14 elements with atomic numbers from 58 (cerium, Ce) to 71 (lutetium, Lu) (126)

lattice energy the energy released when one mole of an ionic crystalline compound is formed from gaseous ions (178)

law of conservation of mass mass is neither created nor destroyed during ordinary chemical or physical reactions (66)

law of definite proportions a chemical compound contains the same elements in exactly the same proportions by mass regardless of the size of the sample or the source of the compound (66)

law of multiple proportions if two or more different compounds are composed of the same two elements, then the ratio of the masses of the second element combined with a certain mass of the first element is always a ratio of small whole numbers (66)

Le Châtelier's principle when a system at equilibrium is disturbed by application of a stress, it attains a new equilibrium position that minimizes the stress (374)

Lewis acid an atom, ion, or molecule that accepts an electron pair to form a covalent bond (467)

Lewis acid-base reaction the formation of one or more covalent bonds between an electron-pair donor and an electron-pair acceptor (468)

Lewis base an atom, ion, or molecule that donates an electron pair to form a covalent bond (468)

Lewis structure a formula in which atomic symbols represent nuclei and inner-shell electrons, dot-pairs or dashes between two atomic symbols represent electron pairs in covalent bonds, and dots adjacent to only one atomic symbol represent unshared electrons (171)

limiting reactant the reactant that limits the amounts of the other reactants that can combine—and the amount of product that can form—in a chemical reaction (288)

line-emission spectrum a series of specific wavelengths of emitted light created when the visible portion of light from excited atoms is shined through a prism (94)

liquid the state of matter in which the substance has a definite volume but an indefinite shape (12)

London dispersion force an intermolecular attraction resulting from the constant motion of electrons and the creation of instantaneous dipoles (193)

lone pair a pair of electrons that is not involved in bonding and that belongs exclusively to one atom (171)

M

magic numbers the numbers of nucleons that represent completed nuclear energy levels—2, 8, 20, 28, 50, 82, and 126 (703)

magnetic quantum number the quantum number that indicates the orientation of an orbital around the nucleus (102)

main-group element an element in the *s*-block or *p*-block (136)

malleability the ability of a substance to be hammered or beaten into thin sheets (182)

mass a measure of the amount of matter (10)

mass defect the difference between the mass of an atom and the sum of the masses of its protons, neutrons, and electrons (701)

mass number the total number of protons and neutrons in the nucleus of an isotope (76)

matter anything that has mass and takes up space (10)

melting the physical change of a solid to a liquid by the addition of heat (368)

melting point the temperature at which a solid becomes a liquid (368)

metal an element that is a good conductor of heat and electricity (22)

metallic bonding chemical bonding that results from the attraction between metal atoms and the surrounding sea of electrons (181)

metalloid an element that has some characteristics of metals and some characteristics of nonmetals (24)

millimeters of mercury a common unit of pressure (311)

miscible liquid solutes and solvents that are able to dissolve freely in one another in any proportion (406)

mixture a blend of two or more kinds of matter, each of which retains its own identity and properties (15)

model an explanation of how phenomena occur and how data or events are related (31)

moderator a material used to slow down the fast neutrons produced by fission (718)

molal boiling-point constant the boiling-point elevation of a solvent in a 1-molal solution of a nonvolatile, nonelectrolyte solute (440)

molal freezing-point constant the freezing-point depression of the solvent in a 1-molal solution of a nonvolatile, nonelectrolyte solute (438)

molality the concentration of a solution expressed in moles of solute per kilogram of solvent (416)

molar heat of formation the heat released or absorbed when one mole of a compound is formed by the combination of its elements (517)

molar heat of fusion the amount of heat energy required to melt one mole of solid at its melting point (380)

molar heat of vaporization the amount of heat energy needed to vaporize one mole of liquid at its boiling point (379)

molar mass the mass of one mole of a pure substance (81)

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molarity the number of moles of solute in one liter of solution (412)

mole the amount of a substance that contains as many particles as there are atoms in exactly 12 g of carbon-12 (81)

mole ratio a conversion factor that relates the amounts in moles of any two substances involved in a chemical reaction (276)

molecular compound a chemical compound whose simplest units are molecules (164)

molecular formula a formula showing the types and numbers of atoms combined in a single molecule of a molecular compound (164)

molecular polarity the uneven distribution of molecular charge (183)

molecule a neutral group of atoms that are held together by covalent bonds (164)

monatomic ion an ion formed from a single atom (204)

monomer a small unit that joins with others to make a polymer (685)

monoprotic acid an acid that can donate only one proton (hydrogen ion) per molecule (465)

multiple bond a double or triple bond (173)

N

natural gas a fossil fuel composed primarily of alkanes containing one to four carbon atoms (643)

net ionic equation an equation that includes only those compounds and ions that undergo a chemical change in a reaction in an aqueous solution (429)

neutralization the reaction of hydronium ions and hydroxide ions to form water molecules (475)

newton the SI unit for force; the force that will increase the speed of a one kilogram mass by one meter per second each second it is applied (309)

noble gas a Group 18 element (helium, neon, argon, krypton, xenon, and radon) (111)

noble-gas configuration an outer main energy level fully occupied, in most cases, by eight electrons (112)

nomenclature a naming system (206)

nonelectrolyte a substance that dissolves in water to give a solution that does not conduct an electric current (400)

nonmetal an element that is a poor conductor of heat and electricity (23)

nonpolar-covalent bond a covalent bond in which the bonding electrons are shared equally by the bonded atoms, resulting in a balanced distribution of electrical charge (162)

nonvolatile substance a substance that has little tendency to become a gas under existing conditions (436)

nuclear binding energy the energy released when a nucleus is formed from nucleons (702)

nuclear fission a process in which a very heavy nucleus splits into more-stable nuclei of intermediate mass (717)

nuclear force a short-range proton-neutron, proton-proton, or neutron-neutron force that holds the nuclear particles together (74)

nuclear fusion the combining of light-mass nuclei to form a heavier, more stable nucleus (719)

nuclear power plant a facility that uses heat from nuclear reactors to produce electrical energy (718)

nuclear radiation the particles or electromagnetic radiation emitted from the nucleus during radioactive decay (705)

nuclear reaction a reaction that affects the nucleus of an atom (704)

nuclear reactor a device that uses controlled-fission chain reactions to produce energy or radioactive nuclides (718)

nuclear shell model nucleons exist in different energy levels, or shells, in the nucleus (703)

nuclear waste radioactive products of fission and fusion reactions (716)

nucleon a proton or neutron (701)

nuclide the general term for any isotope of any element (77); another term for an atom that is identified by the number of protons and neutrons in its nucleus (701)

O

octane rating a measure of a fuel's burning efficiency and its antiknock properties (645)

octet rule chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has an octet of electrons in its highest occupied energy level (169)

orbital a three-dimensional region around the nucleus that indicates the probable location of an electron (100)

organic compound a covalently bonded compound containing carbon, excluding carbonates and oxides (629)

osmosis the movement of solvent through a semipermeable membrane from the side of lower solute concentration to the side of higher solute concentration (442)

osmotic pressure the external pressure that must be applied to stop osmosis (442)

oxidation a reaction in which the atoms or ions of an element experience an increase in oxidation state (592)

oxidation number a number assigned to an atom in a molecular compound or molecular ion that indicates the general distribution of electrons among the bonded atoms (216)

oxidation-reduction reaction any chemical process in which elements undergo changes in oxidation number (593)

oxidation state a number assigned to an atom in a molecular compound or ion that indicates the general distribution of electrons among the bonded atoms (216)

oxidized having experienced an increase in oxidation number (592)

oxidizing agent a substance that has the potential to cause another substance to be oxidized (602)

oxyacid an acid that is a compound of hydrogen, oxygen, and a third element, usually a non-metal (455)

oxyanion a polyatomic ion that contains oxygen (209)

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P

pH the negative of the common logarithm of the hydronium ion concentration of a solution (485)

pH meter a device used to determine the pH of a solution by measuring the voltage between the two electrodes that are placed in the solution (494)

pOH the negative of the common logarithm of the hydroxide ion concentration of a solution (485)

parent nuclide the heaviest nuclide of each decay series (710)

partial pressure the pressure of each gas in a mixture (322)

pascal the pressure exerted by a force of one newton acting on an area of one square meter (311)

Pauli exclusion principle no two electrons in the same atom can have the same set of four quantum numbers (106)

percent error a value calculated by subtracting the experimental value from the accepted value, dividing the difference by the accepted value, and then multiplying by 100 (45)

percent yield the ratio of the actual yield to the theoretical yield, multiplied by 100 (293)

percentage composition the percentage by mass of each element in a compound (227)

period a horizontal row of elements in the periodic table (21)

periodic law the physical and chemical properties of the elements are periodic functions of their atomic numbers (125)

periodic table an arrangement of the elements in order of their atomic numbers so that elements with similar properties fall in the same column, or group (125)

petroleum a complex mixture of different hydrocarbons that varies greatly in composition (643)

phase any part of a system that has uniform composition and properties (373)

phase diagram a graph of pressure versus temperature that shows the conditions under which the phases of a substance exist (381)

photoelectric effect the emission of electrons from a metal when light shines on the metal (93)

photon a particle of electromagnetic radiation that has zero rest mass and carries a quantum of energy (94)

physical change a change in a substance that does not involve a change in the identity of the substance (12)

physical property a characteristic that can be observed or measured without changing the identity of the substance (11)

plasma a high-temperature physical state of matter in which atoms lose their electrons (12)

polar having an uneven distribution of charge (162)

polar-covalent bond a covalent bond in which the bonded atoms have an unequal attraction for the shared electrons (162)

polyatomic ion a charged group of covalently bonded atoms (180)

polymer a large molecule made of many small units joined to each other through organic reactions (685)

polyprotic acid an acid that can donate more than one proton per molecule (465)

positron a particle that has the same mass as an electron but that has a positive charge, and is emitted from the nucleus during some kinds of radioactive decay (706)

precipitate a solid that is produced as a result of a chemical reaction in solution and that separates from the solution (242)

precision the closeness of a set of measurements of the same quantity made in the same way (44)

pressure the force per unit area on a surface (308)

primary amine an organic compound in which one hydrogen atom in an ammonia molecule has been replaced by an alkyl group (677)

primary standard a highly purified solid compound used to check the concentration of a known solution in a titration (499)

principal quantum number the quantum number that indicates the main energy level occupied by the electron (101)

product a substance that is formed by a chemical change (13)

pure substance a substance that has a fixed composition and differs from a mixture in that every sample of a given pure substance has exactly the same characteristic properties and composition (17)

Q

quantity something that has magnitude, size, or amount (33)

quantum the minimum quantity of energy that can be gained or lost by an atom (93)

quantum number a number that specifies the properties of atomic orbitals and the properties of electrons in orbitals (101)

quantum theory a mathematical description of the wave properties of electrons and other very small particles (99)

R

radioactive dating the process by which the approximate age of an object is determined based on the amount of certain radioactive nuclides present (715)

radioactive decay the spontaneous disintegration of a nucleus into a slightly lighter and more stable nucleus, accompanied by emission of particles, electromagnetic radiation, or both (705)

radioactive nuclide an unstable nucleus that undergoes radioactive decay (705)

radioactive tracer a radioactive atom that is incorporated into a substance so that movement of the substance can be followed by a radiation detector (715)

rate-determining step the slowest-rate step for a chemical reaction (543)

rate law an equation that relates the reaction rate and concentrations of reactants (542)

reactant a substance that reacts in a chemical change (13)

reaction mechanism the step-by-step sequence of reactions by which the overall chemical change occurs (531)

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reaction rate the change in concentration of reactants per unit time as a reaction proceeds (538)

reaction stoichiometry calculations involving the mass relationships between reactants and products in a chemical reaction (275)

real gas a gas that does not behave completely according to the assumptions of the kinetic-molecular theory (306)

redox reaction any chemical process in which elements undergo changes in oxidation number (593)

reduced having experienced a decrease in oxidation state (593)

reducing agent a substance that has the potential to cause another substance to be reduced (602)

reduction a reaction in which the oxidation state of an element decreases (593)

reduction potential the measurement of the tendency for a half-reaction to occur as a reduction half-reaction in an electrochemical cell (613)

rem the quantity of ionizing radiation that does as much damage to human tissue as is done by 1 roentgen of high-voltage X rays (713)

resonance the bonding in molecules or ions that cannot be correctly represented by a single Lewis structure (175)

reversible reaction a chemical reaction in which the products re-form the original reactants (246)

roentgen a unit used to measure nuclear radiation; equal to the amount of radiation that produces 2×10^9 ion pairs when it passes through 1 cm^3 of dry air (713)

S

salt an ionic compound composed of a cation and the anion from an acid (215); an ionic compound composed of a cation from a base and an anion from an acid (473)

saturated hydrocarbon a hydrocarbon in which each carbon atom in the molecule forms four single covalent bonds with other atoms (634)

saturated solution a solution that contains the maximum amount of dissolved solute (403)

scientific method a logical approach to solving problems by observing and collecting data, formulating hypotheses, testing hypotheses, and formulating theories that are supported by data (29)

scientific notation numbers written in the form $M \times 10^n$ where the factor M is a number greater than or equal to 1 but less than 10 and n is a whole number (50)

scintillation counter an instrument that converts scintillating light to an electric signal for detecting radiation (714)

secondary amine an organic compound in which two hydrogen atoms of an ammonia molecule have been replaced by alkyl groups (677)

self-ionization of water a process in which two water molecules produce a hydronium ion and a hydroxide ion by transfer of a proton (481)

semipermeable membrane a membrane that allows the movement of some particles while blocking the movement of others (442)

shielding radiation-absorbing material that is used to decrease radiation exposure from nuclear reactors, especially gamma rays (718)

SI *(Le Système International d'Unités)* the measurement system accepted worldwide (33)

significant figure any digit in a measurement that is known with certainty plus one final digit, which is somewhat uncertain or is estimated (46)

single bond a covalent bond produced by the sharing of one pair of electrons between two atoms (171)

single-replacement reaction a reaction in which one element replaces a similar element in a compound (261)

solid the state of matter in which the substance has definite volume and definite shape (12)

solubility the amount of a substance required to form a saturated solution with a specific amount of solvent at a specified temperature (404)

solubility product constant the product of the molar concentrations of ions of a substance in a saturated solution, each raised to the power that is the coefficient of that ion in the chemical equation (578)

soluble capable of being dissolved (395)

solute the substance dissolved in a solution (396)

solution a homogeneous mixture of two or more substances in a single phase (396)

solution equilibrium the physical state in which the opposing processes of dissolution and crystallization of a solute occur at equal rates (402)

solvated a solute particle that is surrounded by solvent molecules (409)

solvent the dissolving medium in a solution (396)

specific heat the amount of heat energy required to raise the temperature of one gram of substance by one Celsius degree (1°C) or one kelvin (1 K) (512)

spectator ion an ion that does not take part in a chemical reaction and is found in solution both before and after the reaction (429)

spin quantum number the quantum number that has only two possible values, +1/2 and –1/2, which indicate the two fundamental spin states of an electron in an orbital (104)

standard electrode potential a half-cell potential measured relative to a potential of zero for the standard hydrogen electrode (614)

standard molar volume of a gas the volume occupied by one mole of a gas at STP, 22.414 10 L (335)

standard solution a solution that contains a precisely known concentration of a solute (499)

standard temperature and pressure the agreed-upon standard conditions of exactly 1 atm pressure and 0°C (312)

strong acid an acid that ionizes completely in aqueous solution (460)

strong electrolyte any compound of which all or almost all of the dissolved compound exists as ions in aqueous solution (432)

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structural formula a formula that indicates the number and types of atoms present in a molecule and also shows the bonding arrangement of the atoms (630); a formula that indicates the kind, number, arrangement, and bonds but not the unshared electron pairs of the atoms in a molecule (171)

structural isomers isomers in which the atoms are bonded together in different orders (631)

sublimation the change of state from a solid directly to a gas (380)

substitution reaction a reaction in which one or more atoms replace another atom or group of atoms in a molecule (682)

supercooled liquid a substance that retains certain liquid properties even at temperatures at which it appears to be solid (368)

supersaturated solution a solution that contains more dissolved solute than a saturated solution contains under the same conditions (403)

surface tension a force that tends to pull adjacent parts of a liquid's surface together, thereby decreasing surface area to the smallest possible size (365)

suspension a mixture in which the particles in the solvent are so large that they settle out unless the mixture is constantly stirred or agitated (397)

synthesis reaction a reaction in which two or more substances combine to form a new compound (256)

system a specific portion of matter in a given region of space that has been selected for study during an experiment or observation (29)

T

temperature a measure of the average kinetic energy of the particles in a sample of matter (511)

tertiary amine an organic compound in which all three hydrogen atoms of an ammonia molecule have been replaced by alkyl groups (677)

theoretical yield the maximum amount of product that can be produced from a given amount of reactant (293)

theory a broad generalization that explains a body of facts or phenomena (31)

thermochemical equation an equation that includes the quantity of heat released or absorbed during the reaction as written (515)

thermochemistry the study of the changes in heat energy that accompany chemical reactions and physical changes (511)

thermoplastic polymer a polymer that melts when heated and can be reshaped many times (685)

thermosetting polymer a polymer that does not melt when heated but keeps its original shape (685)

titration the controlled addition and measurement of the amount of a solution of known concentration required to react completely with a measured amount of a solution of unknown concentration (497)

transition element one of the *d*-block elements that is a metal, with typical metallic properties (134)

transition interval the pH range over which an indicator changes color (494)

transmutation a change in the identity of a nucleus as a result of a change in the number of its protons (704)

transuranium element an element with more than 92 protons in its nucleus (712)

triple bond a covalent bond produced by the sharing of three pairs of electrons between two atoms (173)

triple point the temperature and pressure conditions at which the solid, liquid, and vapor of a substance can coexist at equilibrium (381)

triprotic acid an acid able to donate three protons per molecule (466)

U

unit cell the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice (369)

unsaturated hydrocarbon a hydrocarbon in which not all carbons have four single covalent bonds (647)

unsaturated solution a solution that contains less solute than a saturated solution under the existing conditions (403)

unshared pair a pair of electrons that is not involved in bonding and that belongs exclusively to one atom (171)

V

valence electron an electron that is available to be lost, gained, or shared in the formation of chemical compounds (150)

vaporization the process by which a liquid or solid changes to a gas (365)

volatile liquid a liquid that evaporates readily (377)

voltaic cell an electrochemical cell in which the redox reaction occurs naturally and produces electrical energy (608)

volume the amount of space occupied by an object (37)

VSEPR theory repulsion between the sets of valence-level electrons surrounding an atom causes these sets to be oriented as far apart as possible (183)

vulcanization a cross-linking process between adjacent polyisoprene molecules that occurs when the molecules are heated with sulfur atoms (688)

W

wavelength the distance between corresponding points on adjacent waves (91)

weak acid an acid that is a weak electrolyte (460)

weak electrolyte a compound of which a relatively small amount of the dissolved compound exists as ions in an aqueous solution (433)

weight a measure of the gravitational pull on matter (35)

word equation an equation in which the reactants and products in a chemical reaction are represented by words (243)

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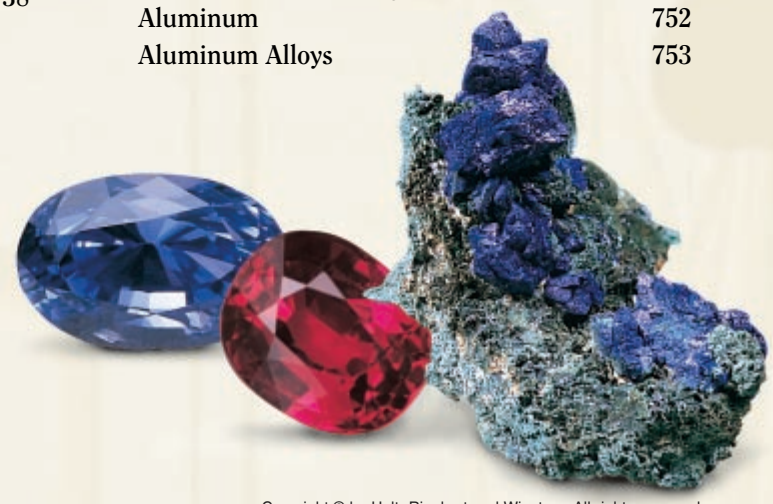

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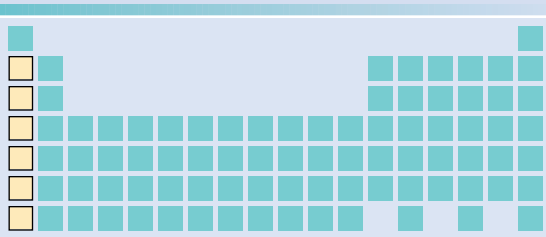
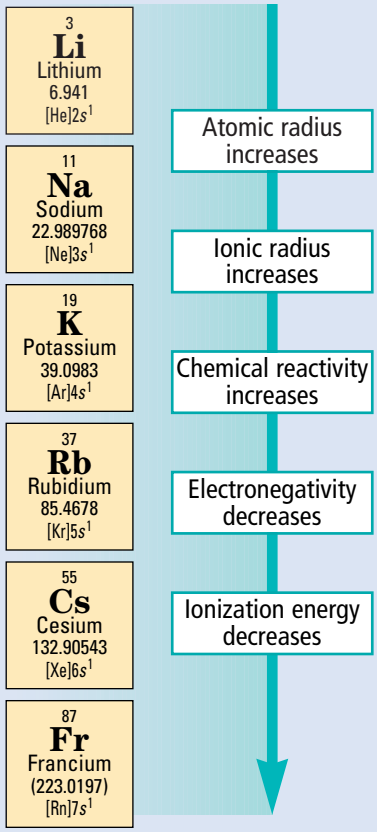
GROUP 1
ALKALI METALS



CHARACTERISTICS

- do not occur in nature as elements
- are reactive metals obtained by reducing the 1+ ions in their natural compounds
- are stored under kerosene or other hydrocarbon solvent because they react with water vapor or oxygen in air
- consist of atoms with one electron in the outermost energy level
- form colorless ions, each with a 1+ charge
- form ionic compounds
- form water-soluble bases
- are strong reducing agents
- consist of atoms that have low ionization energies
- are good conductors of electricity and heat
- are ductile, malleable, and soft enough to be cut with a knife
- have a silvery luster, low density, and low melting point



Lithium was discovered in 1817. It is found in most igneous rocks and is used in batteries as an anode because it has a very low reduction potential. Lithium is soft and is stored in oil or kerosene to prevent it from reacting with the air.

Sodium derives its name from the word soda. *It was first isolated in 1807 from the electrolysis of caustic soda, NaOH. Sodium is soft enough to be cut with a knife. It is shiny until it reacts with oxygen, which causes the surface to lose its luster.*

Potassium was first isolated in 1807 from the electrolysis of caustic potash, KOH.

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COMMON REACTIONS

A small piece of potassium dropped into water will react explosively, releasing H_2 to form a strongly basic hydroxide solution. The heat of the reaction ignites the hydrogen gas that is produced.

With Water and Acids to Form Bases and Hydrogen Gas

Example: $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$
Li, K, Rb, and Cs also follow this pattern.

Example: $2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$
Li, K, Rb, and Cs also follow this pattern.

With Halogens to Form Salts

Example: $2Na(s) + F_2(g) \longrightarrow 2NaF(s)$
Li, K, Rb, and Cs also follow this pattern in reacting with F_2, Cl_2, Br_2, and I_2.

With Oxygen to Form Oxides, Peroxides, or Superoxides

Lithium forms an oxide.
$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$

Sodium forms a peroxide.
$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$

Alkali metals with higher molecular masses can form superoxides.
$K(s) + O_2(g) \longrightarrow KO_2(s)$
Rb and Cs also follow this pattern.

Sodium reacts vigorously with chlorine to produce NaCl. Most salts of Group 1 metals are white crystalline compounds.

Alkali-Metal Oxides with Water to Form Bases

Oxides of Na, K, Rb, and Cs can be prepared indirectly. These basic anhydrides form hydroxides in water.

Example: $K_2O(s) + H_2O(l) \longrightarrow 2KOH(aq)$
Li, Na, Rb, and Cs also follow this pattern.

ANALYTICAL TEST

Alkali metals are easily detected by flame tests because each metal imparts a characteristic color to a flame.

When sodium and potassium are both present in a sample, the yellow color of the sodium masks the violet color of the potassium. The violet color can be seen only when the combined sodium-potassium flame is viewed through a cobalt-blue glass. The glass blocks the yellow flame of sodium and makes it possible to see the violet flame of potassium.

Lithium

Sodium

Potassium

Rubidium

Cesium

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PROPERTIES OF THE GROUP 1 ELEMENTS

	Li	Na	K	Rb	Cs	Fr
Melting point (°C)	180.5	97.8	63.25	38.89	28.5	27
Boiling point (°C)	1342	882.9	760	691	668	—
Density (g/cm^3)	0.534	0.971	0.862	1.53	1.87	—
Ionization energy (kJ/mol)	520	496	419	403	376	—
Atomic radius (pm)	152	186	227	248	265	270
Ionic radius (pm)	76	102	138	152	167	180
Common oxidation number in compounds	+1	+1	+1	+1	+1	—
Crystal structure	bcc*	bcc	bcc	bcc	bcc	—
Hardness (Mohs' scale)	0.6	0.4	0.5	0.3	0.2	—

*body-centered cubic

APPLICATION *Technology*

Sodium Vapor Lighting

The flame test for sodium shows a bright line between 589.0 and 589.5 nm, which is the yellow range of the emission spectrum. Sodium can be vaporized at high temperatures in a sealed tube and made to give off light using two electrodes connected to a power source. Sodium vapor lighting is often used along highways and in parking lots because it provides good illumination while using less energy than other types of lighting.

Sodium vapor lighting comes in both low-pressure and high-pressure bulbs. Low-pressure lamps reach an internal temperature of 270°C to vaporize the sodium under a pressure of about 1 Pa. High-pressure lamps contain mercury and xenon in addition to sodium. These substances reach an internal temperature of 1100°C under a pressure of about 100 000 Pa. The high-pressure lamp provides a higher light intensity. The design of both types of lamps must take into account the high reactivity of sodium, which increases at high temperatures. Because ordinary glass will react with sodium at 250°C, a special sodium-resistant glass is used for low-pressure lamps. High-pressure lamps use an aluminum oxide material for the column containing the sodium, mercury, and xenon. Both types of lamps contain tungsten electrodes.

The light intensity per watt for sodium vapor lamps far exceeds that of fluorescent lamps, high-pressure mercury vapor lamps, tungsten halogen lamps, and incandescent bulbs.

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APPLICATION *Health*

Electrolyte Balance in the Body

The elements of Group 1 are important to a person's diet and body maintenance because they form ionic compounds, that are present in the body as solutions of the ions. All ions carry an electric charge, so they are electrolyte solutes. Two of the most important electrolyte solutes found in the body are K^+ and Na^+ ions. Both ions facilitate the transmission of nerve impulses and control the amount of water retained by cells.

During situations where the body is losing water rapidly through intense sweating or diarrhea for a prolonged period (more than 5 hours), a sports drink can hydrate the body and restore electrolyte balance.

TABLE 1A Sodium-Potassium Composition of Body Fluids

Cation	Inside cells (mmol/L)	Outside cells or in plasma (mmol/L)
Na^+	12	145
K^+	140	4

The sodium and potassium ion concentrations of body fluids are shown in Table 1A. Sodium ions are found primarily in the fluid outside cells, while potassium ions are largely found in the fluid inside cells. Anions are present in the fluids to balance the electrical charge of the Na^+ and K^+ cations.

Abnormal electrolyte concentrations in blood serum can indicate the presence of disease. The ion concentrations that vary as a result of disease are Na^+, K^+, Cl^-, and HCO_3^-. Sodium ion concentration is a good indicator of the water balance between blood and tissue cells. Unusual potassium ion levels can indicate kidney or gastrointestinal problems. Chloride ion is the anion that balances the positive charge of the sodium ion in the fluid outside the cells. It also diffuses into a cell to maintain normal electrolyte balance when hydrogen carbonate ions diffuse out of the cell into the blood. Table 1B shows medical conditions associated with electrolyte imbalances.

TABLE 1B Electrolyte Imbalances

		Causes of imbalance	
Electrolyte	**Normal range (mmol/L)**	**Excess**	**Deficiency**
Sodium, Na^+	135–145	hypernatremia (increased urine excretion; excess water loss)	hyponatremia (dehydration; diabetes-related low blood pH; vomiting; diarrhea)
Potassium, K^+	3.5–5.0	hyperkalemia (renal failure; low blood pH)	hypokalemia (gastrointestinal conditions)
Hydrogen carbonate, HCO_3^-	24–30	hypercapnia (high blood pH; hypoventilation)	hypocapnia (low blood pH; hyperventilation; dehydration)
Chloride, Cl^-	100–106	hyperchloremia (anemia; heart conditions; dehydration)	hypochloremia (acute infection; burns; hypoventilation)

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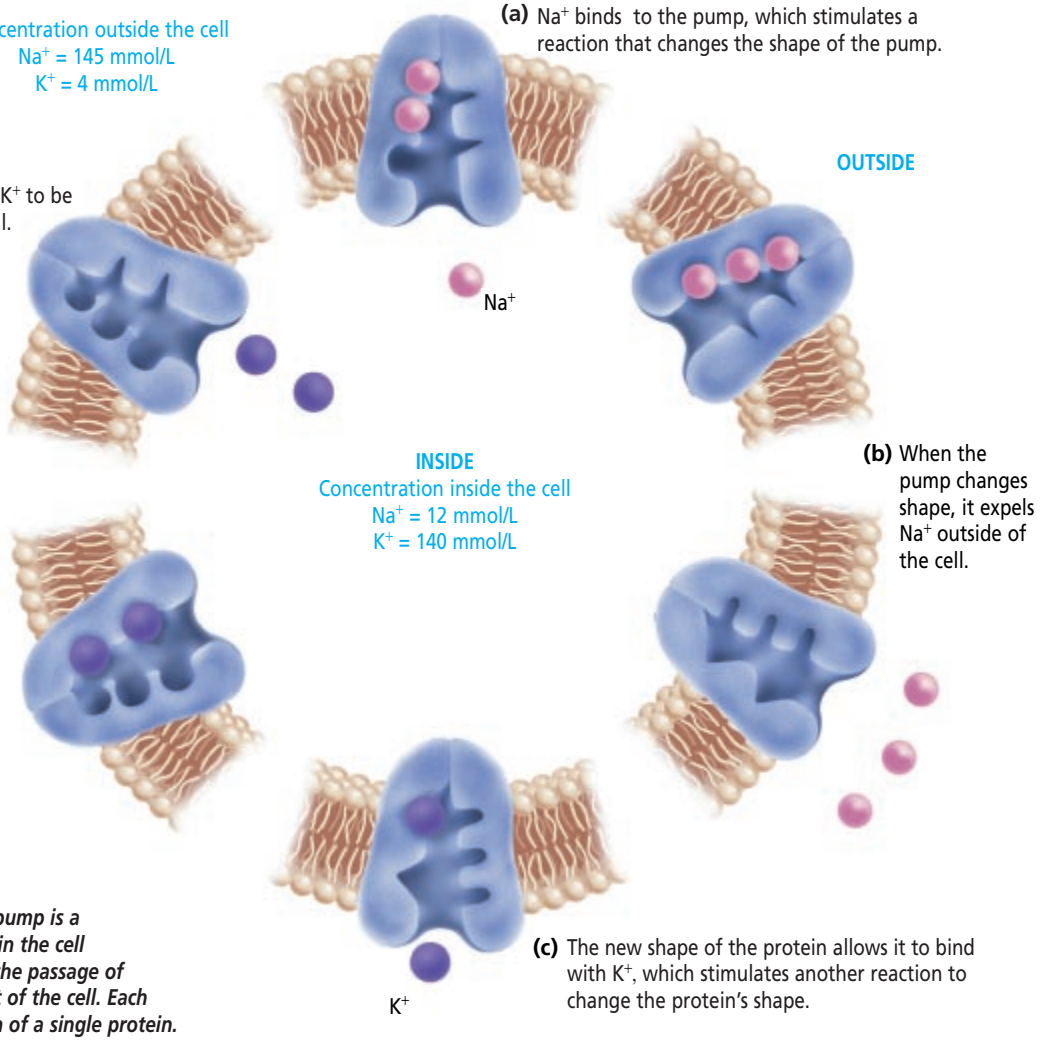
Sodium-Potassium Pump in the Cell Membrane

The process of active transport allows a cell to maintain its proper electrolyte balance. To keep the ion concentrations at the proper levels shown in Table 1B, a sodium-potassium pump embedded in the cell membrane shuttles sodium ions out of the cell across the cell membrane. A model for the action of the sodium-potassium pump is shown below.

Nerve Impulses and Ion Concentration

An uneven distribution of Na^+ and K^+ ions across nerve cell membranes is essential for the normal operation of the nervous system. This uneven distribution of ions creates a voltage across nerve cell membranes. When a nerve cell is stimulated, sodium ions diffuse into the cell from the surrounding fluid, raising voltage across the nerve cell membrane from –70 mV to nearly +60 mV. Potassium ions then diffuse out of the cell into the surrounding fluid, restoring the voltage across the nerve cell membrane to –70 mV. This voltage fluctuation initiates the transmission of a nerve impulse. The amount of Na^+ inside the cell has increased slightly, and the amount of K^+ outside the cell has decreased. But the sodium-potassium pump will restore these ions to their proper concentrations.


Concentration outside the cell
Na+ = 145 mmol/L
K+ = 4 mmol/L
(a) Na+ binds to the pump, which stimulates a reaction that changes the shape of the pump.
OUTSIDE
(d) This reaction causes K+ to be expelled into the cell.
Na+
INSIDE
Concentration inside the cell
Na+ = 12 mmol/L
K+ = 140 mmol/L
(b) When the pump changes shape, it expels Na+ outside of the cell.
K+
(c) The new shape of the protein allows it to bind with K+, which stimulates another reaction to change the protein's shape.

The sodium-potassium pump is a protein embedded within the cell membrane that allows the passage of Na^+ and K^+ into and out of the cell. Each figure depicts the action of a single protein.

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What's your sodium IQ?

Though sodium is an important mineral in your body, a diet that is high in sodium is one of several factors linked to high blood pressure, also known as hypertension. High Na^+ levels cause water retention, which results in increased blood pressure. Sodium is not the direct cause of all hypertension, but reducing sodium levels in the diet can affect individuals with a condition known as salt-sensitive hypertension. Therefore, the Dietary Guidelines for Americans recommend consuming salt and sodium in moderation. Test your knowledge about sodium in foods with the questions below.

1. Which of the following condiments do you think has the lowest salt content?
a. mustard c. catsup e. vinegar
b. steak sauce d. pickles

2. One-fourth of a teaspoon of salt contains about _____ of sodium.
a. 10 mg c. 500 mg e. 1 kg
b. 100 g d. 500 g

3. According to FDA regulations for food product labels, a food labeled *salt-free* must contain less than _____ mg of sodium ion per serving.
a. 100 c. 0.001 e. 0.00005
b. 5 d. 0.005

4. The Nutrition Facts label for a particular food reads "Sodium 15 mg." This is the amount of sodium ion per _____.
a. package c. serving e. RDA
b. teaspoon d. ounce

5. The recommended average daily intake of sodium ion for adults is 2400 mg. For a low-sodium diet the intake should be _____.
a. 200 mg c. 750 mg e. 150 mg
b. 2000 mg d. 500 mg

6. Each of the following ingredients can be found in the ingredients lists for some common food products. Which ones indicate that the product contains sodium?
a. trisodium phosphate d. sodium sulfate
b. sodium bicarbonate e. MSG
c. sodium benzoate f. baking soda

7. Which of the following spices is NOT a salt substitute?
a. caraway seeds d. ginger
b. dill e. onion salt
c. mace

8. Most salt in the diet comes from salting foods too heavily at the dinner table.
a. true b. false

9. Which of the following foods are high in sodium?
a. potato chips c. doughnuts e. figs
b. pizza d. banana

10. Your body requires about 200 mg of sodium ion, or 500 mg of salt, per day. Why do these numbers differ?

Answers 1. e; 2. c; 3. b; 4. c; 5. c; 6. all of them; 7. e; 8. b, processed foods can contain very high levels of sodium; 9. a, b, c; 10. Salt is not pure sodium.

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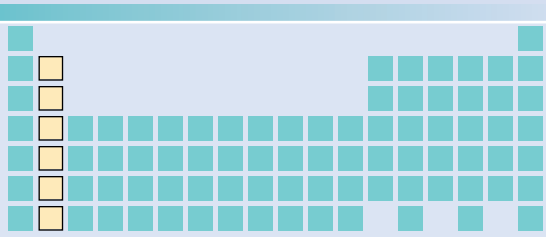
GROUP 2
ALKALINE EARTH METALS



CHARACTERISTICS

- do not occur naturally in their elemental state
- occur most commonly as the carbonates, phosphates, silicates, and sulfates
- occur naturally as compounds that are either insoluble or only slightly soluble in water
- consist of atoms that contain two electrons in their outermost energy level
- consist of atoms that tend to lose two electrons per atom, forming ions with a 2+ charge
- are less reactive than alkali metals
- form ionic compounds primarily
- react with water to form bases and hydrogen gas
- are good conductors of heat and electricity
- are ductile and malleable
- have a silvery luster
- include the naturally radioactive element radium

4 Be Beryllium 9.012182 $[He]2s^2$	Atomic radius increases
12 Mg Magnesium 24.3050 $[Ne]3s^2$	Ionic radius increases
20 Ca Calcium 40.078 $[Ar]4s^2$	Chemical reactivity increases
38 Sr Strontium 87.62 $[Kr]5s^2$	Electronegativity decreases
56 Ba Barium 137.327 $[Xe]6s^2$	Ionization energy decreases
88 Ra Radium (226.0254) $[Rn]7s^2$	

Calcium carbonate is a major component of marble.

Beryllium is found in the mineral compound beryl. Beryl crystals include the dark green emerald and the blue-green aquamarine. The colors of these gems come from other metal impurities.

The mineral dolomite, $CaCO_3 \cdot MgCO_3$, is a natural source of both calcium and magnesium.

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COMMON REACTIONS

With Water to Form Bases and Hydrogen Gas

Example: $Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + H_2(g)$

Ca, Sr, and Ba also follow this pattern.

With Acids to Form Salts and Hydrogen Gas

Example: $Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$

Be, Ca, Sr, and Ba also follow this pattern.

With Halogens to Form Salts

Example: $Mg(s) + F_2(g) \longrightarrow MgF_2(s)$

Ca, Sr, and Ba also follow this pattern in reacting with F_2, Cl_2, Br_2, and I_2.

Calcium reacts with water to form hydrogen gas.

With Oxygen to Form Oxides or Peroxides

Magnesium forms an oxide.

$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

Be and Ca also follow this pattern.

Strontium forms a peroxide.

$Sr(s) + O_2(g) \longrightarrow SrO_2(s)$

Ba also reacts in this way.

With Hydrogen to Form Hydrides

Example: $Mg(s) + H_2(g) \longrightarrow MgH_2(s)$

Ca, Sr, and Ba also follow this pattern.

With Nitrogen to Form Nitrides

Example: $3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

Be and Ca also follow this pattern.

Magnesium burns in air to form MgO and Mg_3N_2.

Magnesium reacts with HCl to produce $MgCl_2$(aq).

ANALYTICAL TEST

Flame tests can be used to identify three of the alkaline earth elements. The colors of both calcium and strontium can be masked by the presence of barium, which produces a green flame.

Calcium

Strontium

Barium

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PROPERTIES OF THE GROUP 2 ELEMENTS

	Be	Mg	Ca	Sr	Ba	Ra
Melting point (°C)	1287 ± 5	649	839 ± 2	769	725	700
Boiling point (°C)	2467	1107	1484	1384	1640	1737
Density (g/cm^3)	1.85	1.74	1.54	2.6	3.51	—
Ionization energy (kJ/mol)	900	738	590	550	503	509
Atomic radius (pm)	112	160	197	215	222	220
Ionic radius (pm)	45	72	100	118	136	148
Common oxidation number in compounds	+2	+2	+2	+2	+2	+2
Crystal structure	hcp*	hcp	fcc**	fcc	bcc	bcc
Hardness (Mohs' scale)	4.0	2.0	1.5	1.8	1.5	—

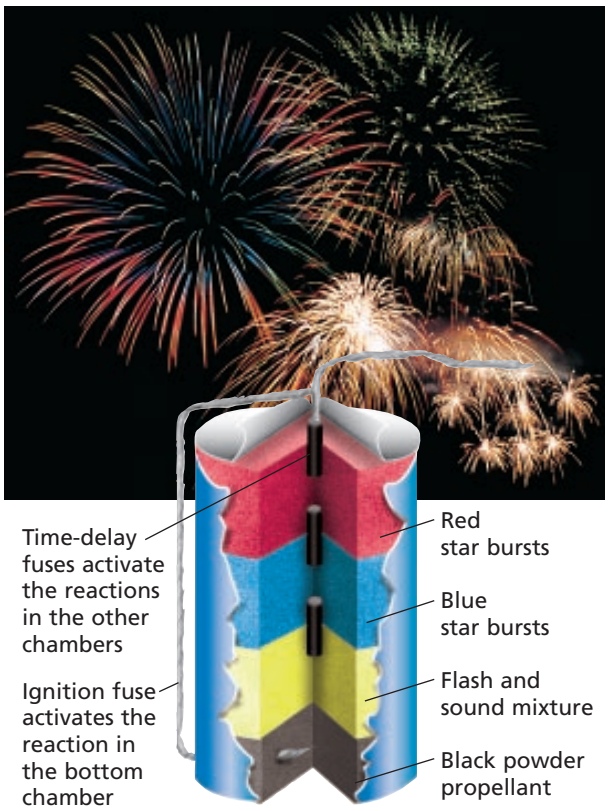
*hexagonal close-packed **face-centered cubic

APPLICATION *Technology*

Fireworks

Fireworks are made from pyrotechnics—chemical substances that produce light and smoke when they are ignited. Pyrotechnics are also used in flares, smoke bombs, explosives, and matches. An aerial fireworks device is a rocket made of a cylinder, chemicals inside the cylinder, and fuses attached to the cylinder. The illustration on the right shows how the device works. The lift charge at the bottom of the cylinder consists of a small amount of black gunpowder. When the side fuse ignites the gunpowder, it explodes like a small bomb. The gunpowder consists of potassium nitrate, charcoal, and sulfur. When these three chemicals react with one another, they produce gases. In this case, the gases produced are carbon monoxide, carbon dioxide, sulfur dioxide, and nitrogen monoxide. These hot gases expand very rapidly, providing the thrust that lifts the rocket into the sky.

About the time the shell reaches its maximum altitude and minimum speed, the time fuse ignites the chemicals contained in the cylinder. The chemicals inside the cylinder determine the color of the burst.


Time-delay fuses activate the reactions in the other chambers
Ignition fuse activates the reaction in the bottom chamber
Red star bursts
Blue star bursts
Flash and sound mixture
Black powder propellant

The cylinder of a multiple-burst rocket contains separate reaction chambers connected by fuses. A common fuse ignites the propellant and the time-delay fuse in the first reaction chamber.

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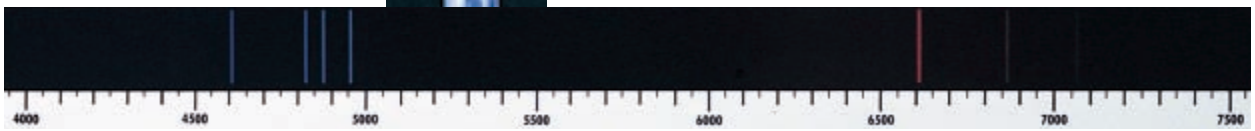
Chemical Composition and Color

One of the characteristics of fireworks that we enjoy most is their variety of rich colors. These colors are created in much the same way as the colors produced during a flame test. In a fireworks device, the chloride salt is heated to a high temperature, causing the excited atoms to give off a burst of light. The color of light produced depends on the metal used. The decomposition of barium chloride, $BaCl_2$, for example, produces a burst of green light, whereas strontium chloride, $SrCl_2$, releases red light.

People who design fireworks combine artistry with a technical knowledge of chemical properties. They have found ways to combine different colors within a single cylinder and to make parts of the cylinder explode at different times. Fireworks designers have a technical knowledge of projectile motion that is used to determine the height, direction, and angle at which a fireworks device will explode to produce a fan, fountain, flower, stream, comet, spider, star, or other shape.

Strontium and the Visible Spectrum

When heated, some metallic elements and their compounds emit light at specific wavelengths that are characteristic of the element or compound. Visible light includes wavelengths between about 400 and 700 nanometers. The figure below shows the emission spectrum for strontium. When heated, strontium gives off the maximum amount of visible light at about 700 nanometers, which falls in the red-light region of the visible spectrum.

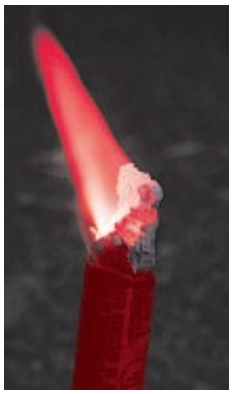


The emission spectrum for strontium shows strong bands in the red region of the visible light spectrum.

Flares

Flares operate on a chemical principle that is different from that of fireworks. A typical flare consists of finely divided magnesium metal and an oxidizing agent. When the flare is ignited, the oxidizing agent reacts with the magnesium metal to produce magnesium oxide. This reaction releases so much energy that it produces a glow like that of the filaments in a light bulb. The brilliant white light produced by the flare is caused by billions of tiny particles of magnesium that glow when they react. If slightly larger particles of magnesium metal are used in the flare, the system glows for a longer period of time because the particles' reaction with the oxidizing agent is slower.

A colored flare can be thought of as a combination of a white flare and a chemical that produces colored light when burned. For example, a red flare can be made from magnesium metal, an oxidizing agent, and a compound of strontium. When the flare is ignited, the oxidizing agent and magnesium metal react, heating the magnesium to white-hot temperatures. The heat from this reaction causes the strontium compound to give off its characteristic red color.



A flare is made up of billions of reacting magnesium particles.

For safety reasons, some fireworks manufacturers store their products in metal sheds separated by sand banks. Also, people who work with fireworks are advised to wear cotton clothing because cotton is less likely than other fabrics to develop a static charge, which can cause a spark and accidentally ignite fireworks.

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APPLICATION *Health*

Calcium: An Essential Mineral in the Diet

Calcium is the most abundant mineral in the body. It is the mineral that makes up a good portion of the teeth and the bone mass of the body. A small percentage of calcium in the body is used in the reactions by which cells communicate and in the regulation of certain body processes. Calcium is so important to normal body functioning that if the calcium level of the blood falls far below normal, hormones signal the release of calcium from bone and signal the gastrointestinal tract to absorb more calcium during the digestion process.

A prolonged diet that is low in calcium is linked to a disease characterized by a decrease in bone mass, a condition called osteoporosis. Reduced bone mass results in brittle bones that fracture easily. Osteoporosis generally occurs later in life and is more prevalent in females. However, because you achieve peak bone mass during the late teens or early twenties, it is critical that your diet meet the recommended requirements to increase your peak bone mass. The recommended dietary intake for calcium is 1000 mg per day. Maintaining that level in the diet along with regular exercise through adulthood are thought to reduce the rate of bone loss later in life. Excess calcium in the diet (consuming more than 2500 mg daily) can interfere with the absorption of other minerals.

Dairy products are generally good sources of calcium.

Magnesium: An Essential Mineral in the Diet

Though magnesium has several functions in the body, one of the more important functions is its role in the absorption of calcium by cells. Magnesium, like sodium and potassium, is involved in the transmission of nerve impulses. Like calcium, magnesium is a component of bone.

A major source of magnesium in the diet is plants. Magnesium is the central atom in the green plant pigment chlorophyll. The structure of chlorophyll in plants is somewhat similar to the structure of heme—the oxygen-carrying molecule in animals. (See page 758 for the heme structure.)

TABLE 2A Good Sources of Calcium in the Diet

Food	Serving size	Calcium present (mg)
Broccoli	6.3 oz	82
Cheddar cheese	1 oz	204
Cheese pizza, frozen	pizza for one	375
Milk, low-fat 1%	8 oz	300
Tofu, regular	4 oz	130
Vegetable pizza, frozen	pizza for one	500
Yogurt, low-fat	8 oz	415
Yogurt, plain whole milk	8 oz	274

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Spinach is a good source of magnesium. Magnesium is the central atom in the green plant pigment chlorophyll. The chlorophyll structure is shown on the right.

The recommended dietary intake of magnesium is 400 mg per day. This is equivalent to just 4 oz of bran cereal. Because magnesium levels are easily maintained by a normal diet, it is unusual for anyone to have a magnesium deficiency. Most magnesium deficiencies are the result of factors that decrease magnesium absorption. People with gastrointestinal disorders, alcohol abusers, and the critically ill are most likely to have these types of absorption problems.

Excess magnesium in the diet is excreted by the kidneys, so there are no cumulative toxic effects.

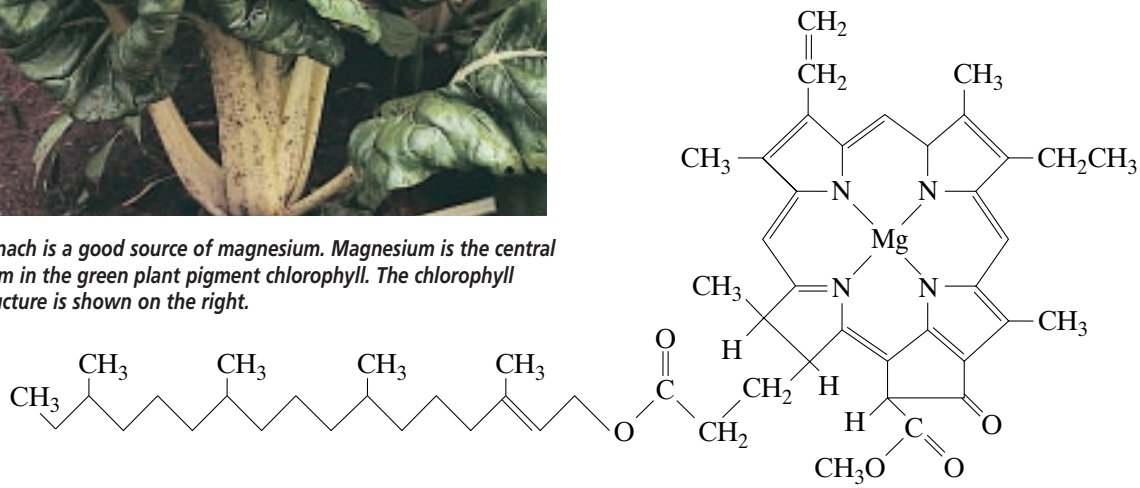

TABLE 2B Good Sources of Magnesium in the Diet

Food	Serving size	Magnesium present (mg)
Barley, raw	1 cup	244
Beef, broiled sirloin	4 oz	36
Cabbage, raw	1 med. head	134
Cashews, dry-roasted	1 oz	74
Chicken, roasted breast	4 oz	31
Lima beans, boiled	1/2 cup	63
Oatmeal	1 oz	39
Potato, baked	7.1 oz	115
Prunes, dried	4 oz	51
Rice bran	8 oz	648
Salmon, canned	4 oz	39
Spinach, raw	10 oz	161

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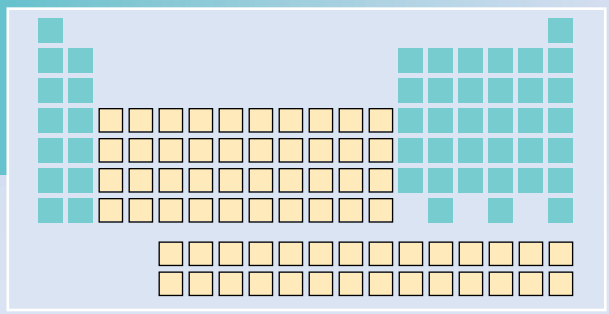
GROUPS 3–12
TRANSITION METALS



CHARACTERISTICS

- consist of metals in Groups 3 through 12
- contain one or two electrons in their outermost energy level
- are usually harder and more brittle than metals in Groups 1 and 2
- have higher melting and boiling points than metals in Groups 1 and 2
- are good conductors of heat and electricity
- are malleable and ductile
- have a silvery luster, except copper and gold
- include radioactive elements with numbers 89 through 112
- include mercury, the only liquid metal at room temperature
- have chemical properties that differ from each other
- tend to have two or more common oxidation states
- often form colored compounds
- may form complex ions

Iron ore is obtained from surface mines. Hematite, Fe_2O_3, is the most common iron ore.

Copper ores are also obtained from surface mines. Copper ore is shown here.

Gold, silver, platinum, palladium, iridium, rhodium, ruthenium, and osmium are sometimes referred to as the noble metals because they are not very reactive. These inert metals are found in coins, jewelry, and metal sculptures.

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COMMON REACTIONS

Because this region of the periodic table is so large, you would expect great variety in the types of reaction characteristics of transition metals. For example, copper oxidizes in air to form the green patina you see on the Statue of Liberty. Copper reacts with concentrated HNO_3 but not with dilute HNO_3. Zinc, on the other hand, reacts readily with dilute HCl. Iron oxidizes in air to form rust, but chromium is generally unreactive in air. Some common reactions for transition elements are shown by the following.

May form two or more different ions

Example: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Example: $Fe(s) \longrightarrow Fe^{3+}(aq) + 3e^-$

May react with oxygen to form oxides

Example: $4Cr(s) + 3O_2(g) \longrightarrow 2Cr_2O_3(s)$

Example: $2Cu(s) + O_2(g) \longrightarrow 2CuO(s)$

May react with halogens to form halides

Example: $Ni(s) + Cl_2(g) \longrightarrow NiCl_2(s)$

May form complex ions

See examples in the lower right.

Copper reacts with oxygen in air.

Copper reacts with concentrated nitric acid.

Zinc reacts with dilute hydrochloric acid.

Soluble iron(III) salts form insoluble $Fe(OH)_3$ when they are reacted with a hydroxide base.

$CrCl_3$ $Cr(NO_3)_3$ $K_2Cr_2O_7$ K_2CrO_4

Chromium has several common oxidation states, represented here by aqueous solutions of its compounds. The violet and green solutions contain chromium in the +3 state, and the yellow and orange solutions contain chromium in the +6 oxidation state.

Complex ions belong to a class of compounds called coordination compounds. Coordination compounds show great variety in colors. Several transition-metal coordination compounds are shown.

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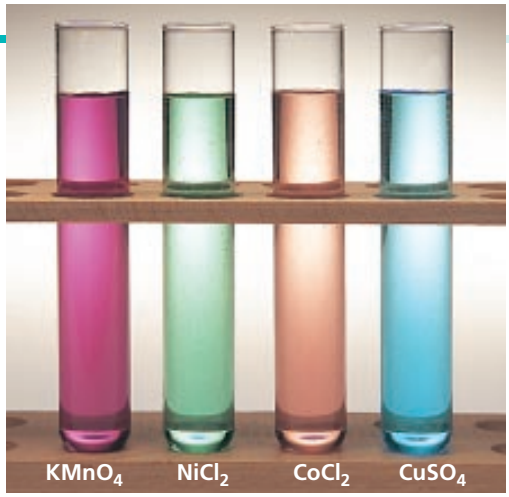
ANALYTICAL TEST

Flame tests are not commonly used to identify transition metals. The presence of a certain transition-metal ion in a solution is sometimes obvious from the solution's color. Some transition-metal ions can be more accurately identified using a procedure called qualitative analysis. **Qualitative analysis** *is the identification of ions by their characteristic reactions.* The transition-metal ions most often identified through qualitative analysis include copper, nickel, zinc, chromium, iron cobalt, cadmium, manganese, and tin. Most tests to identify the presence of an ion in a mixture involve causing the ion to precipitate out of solution. Some of the more dramatic precipitation reactions for transition metals are shown.



Some transition metal ions can be identified by characteristic colors of their salt solutions.

Copper (formation of $[Cu(NH_3)_4](OH)_2$)

Cadmium (formation of CdS)

Zinc (formation of ZnS)

Chromium (formation of $PbCrO_4$)

Iron (formation of $[Fe(SCN)]^{2+}$)

Manganese (formation of MnO_4^-)

Nickel (formation of a nickel dimethylglyoxime complex)

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PROPERTIES OF SOME TRANSITION METALS

	Cr	Fe	Co	Ni	Cu	Zn	Ag	Au	Hg
Melting point (°C)	1857 ± 20	1535	1495	1455	1083	420	962	1064	–38.8
Boiling point (°C)	2672	2750	2870	2732	2567	907	2212	2808 ± 2	356.6
Density (g/cm^3)	7.20	7.86	8.9	8.92	8.96	7.14	10.5	19.3	13.5
Ionization energy (kJ/mol)	653	762	760	737	46	906	731	890	1007
Atomic radius (pm)	128	126	125	124	128	134	144	144	151
Common oxidation numbers	+2, +3, +6	+2, +3	+2, +3	+2	+1, +2	+2	+1	+1, +3	+1, +2

APPLICATION *Geology*

Gemstones and Color

A gemstone is a mineral that can be cut and polished to make gems for an ornament or piece of jewelry. At one time, all gemstones were naturally occurring minerals mined from the Earth's crust. Today, however, chemists can duplicate natural processes to produce artificial gemstones. Amethyst, emerald, jade, opal, ruby, sapphire, and topaz occur naturally and can also be produced synthetically.

The color of a gemstone is determined by the presence of small amounts of one or more transition metals. For example, aluminum oxide, Al_2O_3, often occurs naturally as corundum—a clear, colorless mineral. However, if as few as 1 to 2% of the aluminum ions, Al^{3+}, are replaced by chromium ions, Cr^{3+}, the corundum takes on a reddish color and is known as ruby. If a small fraction of aluminum ions in corundum are replaced by Fe^{3+} and Ti^{3+}, the corundum has a greenish color and is known as emerald. In another variation, if vanadium ions, V^{3+}, replace a few Al^{3+} ions in corundum, the result is a gemstone known as alexandrite. This gemstone appears green in reflected natural light and red in transmitted or artificial light.

Table 3A lists transition metals that are responsible for the colors of various gemstones. The table provides only a general overview, however, as most naturally occurring gemstones occur in a range of hues, depending on the exact composition of the stone.

Artificial Gemstones

In 1902, the French chemist Auguste Verneuil found a way to melt a mixture of aluminum oxide and chromium salts and then cool the mixture very slowly to produce large crystals of reddish aluminum oxide—rubies.

Sapphire

Ruby

Peridot

Garnet

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TABLE 3A Transition Metals and Gemstone Colors

Gemstone	Color	Element
Amethyst	purple	iron
Aquamarine	blue	iron
Emerald	green	iron/titanium
Garnet	red	iron
Peridot	yellow-green	iron
Ruby	red	chromium
Sapphire	blue	iron/titanium
Spinel	colorless to red to black	varies
Turquoise	blue	copper

Verneuil's method, although somewhat modified, is still the one most widely used today for the manufacture of colored gemstones. When magnesium oxide is substituted for aluminum oxide, a colorless spinel-like product is formed. The addition of various transition metals then adds a tint to the spinel that results in the formation of synthetic emerald, aquamarine, tourmaline, or other gemstones. Synthetic gems look very much like their natural counterparts.

Synthetic sapphire

Synthetic ruby

APPLICATION *Technology*

Alloys

An alloy is a mixture of a metal and one or more other elements. In most cases, the second component of the mixture is also a metal.

Alloys are desirable because mixtures of elements usually have properties different from and often superior to the properties of individual metals. For example, many alloys that contain iron are harder, stronger, and more resistant to oxidation than iron itself.

Amalgams are alloys that contain mercury. They are soft and pliable when first produced, but later become solid and hard. Dental fillings were once made of an amalgam of mercury and silver. Concerns about the possible toxicity of mercury led to the development of other filling materials.

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Cast Iron and Steel

The term *steel* applies to any alloy consisting of iron and less than 1.5% carbon, and often other elements. When iron ore is treated with carbon in the form of coke to extract pure iron metal, some of the carbon also reacts with the iron to produce a form of iron carbide known as cementite. The reaction can be represented by the following equation.

$$3Fe + C \longrightarrow Fe_3C$$

Cast iron is a mixture that consists of some pure iron, known as ferrite, some cementite, and some carbon atoms trapped within the crystalline structure of the iron and cementite. The rate at which cast iron is cooled changes the proportion of these three components. If the cast iron is cooled slowly, the ferrite and cementite tend to separate from each other, forming a banded product that is tough but not very hard. However, if the cast iron is cooled quickly, the components of the original mixture cannot separate from each other, forming a product that is both tough and hard.

Stainless steel, which is hard and resists corrosion, is made of iron and chromium (12–30%). The properties of stainless steel make it a suitable alloy for making cutlery and utensils.

TABLE 3B Composition and Uses of Some Alloys

Name of alloy	Composition	Uses
Brass	copper with up to 50% zinc	inexpensive jewelry; hose nozzles and couplings; piping; stamping dies
Bronze	copper with up to 12% tin	coins and medals; heavy gears; tools; electrical hardware
Coin metal	copper: 75% nickel: 25%	United States coins
Duralumin	aluminum: 95% copper: 4% magnesium: 0.5% manganese: <1%	aircraft, boats, railroad cars, and machinery because of its high strength and resistance to corrosion
Nichrome	nickel: 80–85% chromium: 15–20%	heating elements in toasters, electric heaters, etc.
Phosphor bronze	bronze with a small amount of phosphorus	springs, electrical springs, boat propellers
Solder	lead: 50%, tin: 50% or tin: 98%, silver: 2%	joining two metals to each other joining copper pipes
Sterling silver	silver: 92.5% copper: 7.5%	jewelry, art objects, flatware
Type metal	lead: 75–95% antimony: 2–18% tin: trace	used to make type for printing because it expands as it cools

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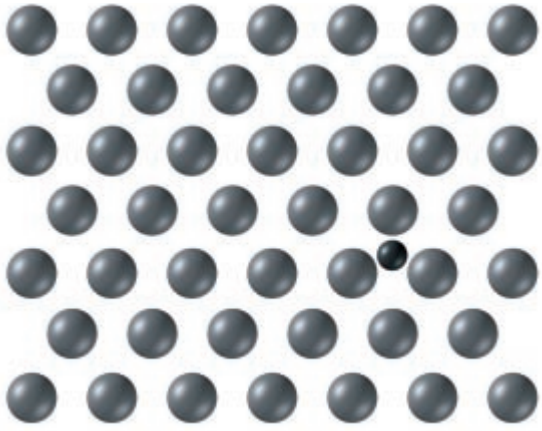
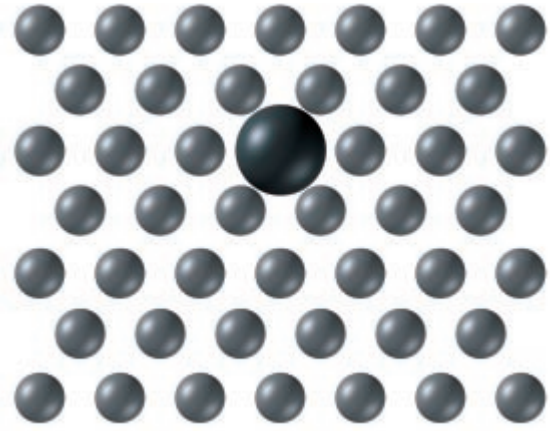


Interstitial crystal
A smaller atom or ion fits into a small space between particles in the array.



Substitutional crystal
A larger atom or ion is substituted for a particle in the array.

Structures and Preparation of Alloys

Alloys generally crystallize in one of two ways, depending on relative sizes of atoms. If the atoms of one of the metals present are small enough to fit into the spaces between the atoms of the second metal, they form an alloy with an interstitial structure (*inter* means "between," and *stitial* means "spaces"). If atoms of the two metals are of similar size or if one is larger, the atoms of one metal can substitute for the atoms of the second metal in its crystalline structure. Such alloys are substitutional alloys. Models for both types of crystals are shown above.

Techniques for making alloys depend on the metals used in the mixture. In some cases, the two metals can simply be melted together to form a mixture. The composition of the mixture often varies within a range, evidence that the final product is indeed a mixture and not a compound. In other cases, one metal may be melted first and the second dissolved in it. Brass is prepared in this way. If copper and zinc were heated together to a high temperature, zinc (bp 907°C) would evaporate before copper (mp 1084°C) melted. Therefore, the copper is melted first, and the zinc is added to it.

Brass has a high luster and resembles gold when cleaned and polished. A brass object can be coated with a varnish to prevent reactions of the alloy with air and water.

Sterling silver is more widely used than pure silver because it is stronger and more durable.

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APPLICATION *The Environment*

Mercury Poisoning

Mercury is the only metal that is liquid at room temperature. It has a very high density compared with most other common transition metals and has a very high surface tension and high vapor pressure. Mercury and many of its compounds must be handled with extreme care because they are highly toxic. Mercury spills are especially hazardous because the droplets scatter easily and are often undetected during cleanup. These droplets release toxic vapors into the air.

Overexposure to mercury vapor or its compounds can occur by absorption through the skin, respiratory tract, or digestive tract. Mercury is a cumulative poison, which means that its concentration in the body increases as exposure increases.

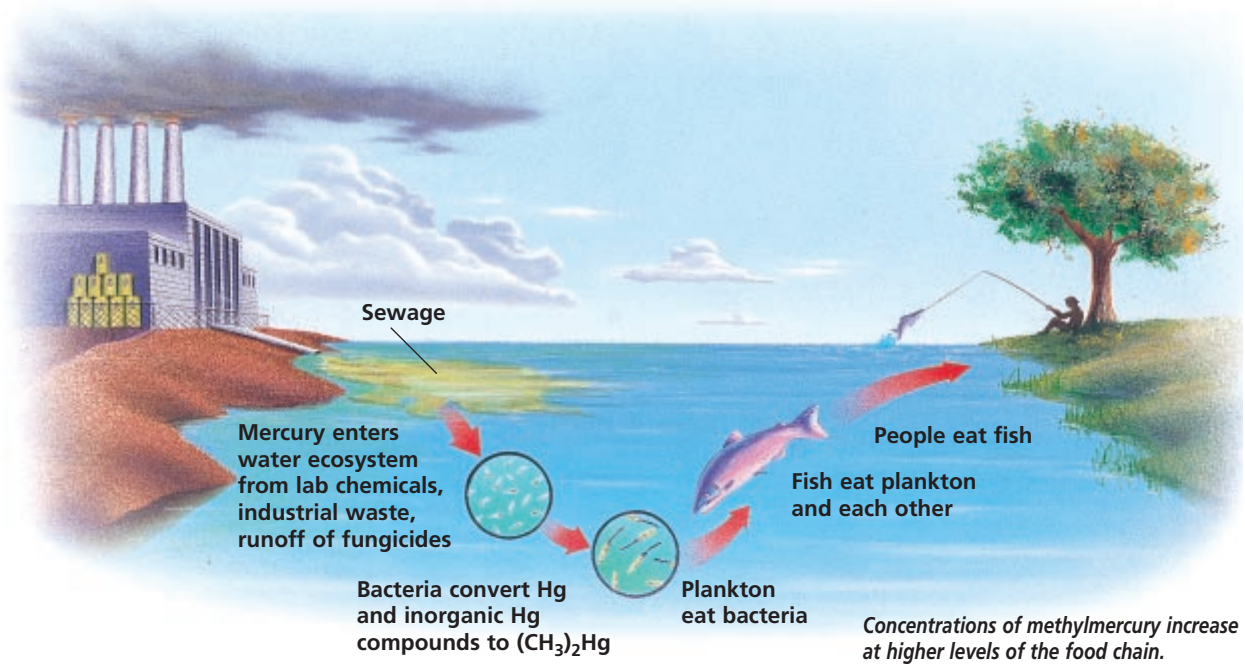
Mercury that enters the body damages the kidneys, heart, and brain. The action of mercury on the brain affects the nervous system. Symptoms of mercury poisoning include numbness, tunnel vision, garbled speech, bleeding and inflammation of the gums, muscle spasms, anemia, and emotional disorders, such as depression, irritability, and personality changes. The saying "mad as a hatter" probably came about because of mercury poisoning. Mercury salts were once routinely used to process the felt used in hats. Hatters often displayed the nerve and mental impairments associated with overexposure to mercury.

Methylmercury in Freshwater Ecosystems

Mercury, Hg, can be found in our environment and in our food supply. Fortunately, the body has some protective mechanisms to deal with trace amounts of mercury. However, levels of mercury and of an organic mercury compound, methylmercury $(CH_3)_2Hg$, are increasing in the environment due to mercury mining operations and runoff from the application of pesticides and fungicides.

Mercury is easily converted to methylmercury by bacteria. Methylmercury is more readily absorbed by cells than mercury itself. As a result, methylmercury accumulates in the food chain as shown in the diagram below. A serious incident of methylmercury poisoning occurred in Japan in the 1950s. People living in Minamata, Japan, were exposed to high levels of methylmercury from eating shellfish.

In the United States there is concern about mercury levels in fish from some freshwater lakes. Though environmental regulations have reduced the level of lake pollutants, it takes time to see a reduction in the concentration of an accumulated poison.


Sewage
Mercury enters water ecosystem from lab chemicals, industrial waste, runoff of fungicides
Bacteria convert Hg and inorganic Hg compounds to $(CH_3)_2Hg$
Plankton eat bacteria
Fish eat plankton and each other
People eat fish

Concentrations of methylmercury increase at higher levels of the food chain.

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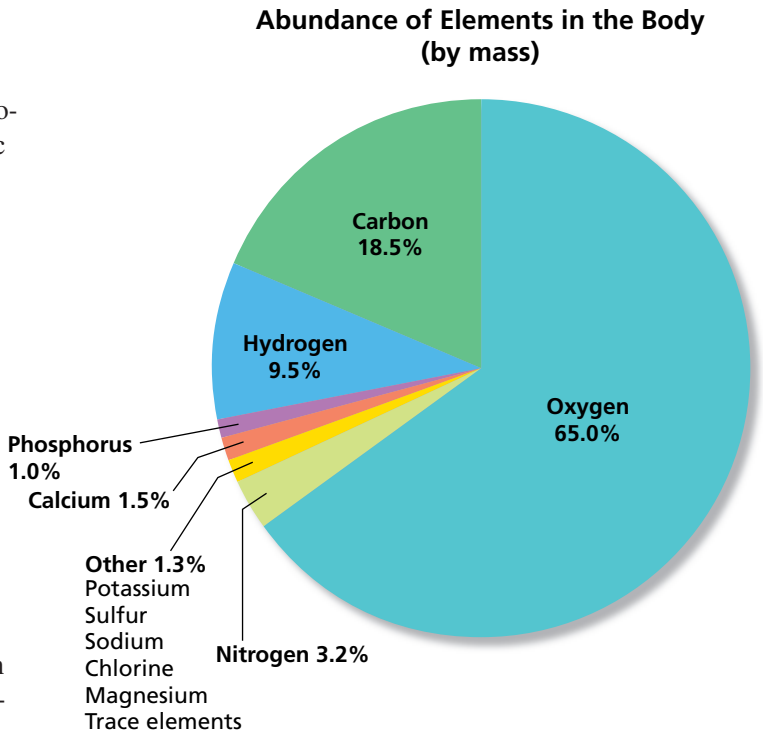
APPLICATION *Health*

Elements in the Body

The four most abundant elements in the body (oxygen, carbon, hydrogen, and nitrogen) are the major components of organic biomolecules, such as carbohydrates, proteins, fats, and nucleic acids. Other elements compose a dietary category of compounds called minerals. Minerals are considered the inorganic elements of the body. Minerals fall into two categories—the major minerals and the trace minerals, or trace elements, as they are sometimes called. Notice in the periodic table below that most elements in the trace elements category of minerals are transition metals.

Trace elements are minerals with dietary daily requirements of 100 mg or less. They are found in foods derived from both plants and animals. Though these elements are present in very small quantities, they perform a variety of essential functions in the body, as shown in Table 3C on the next page.



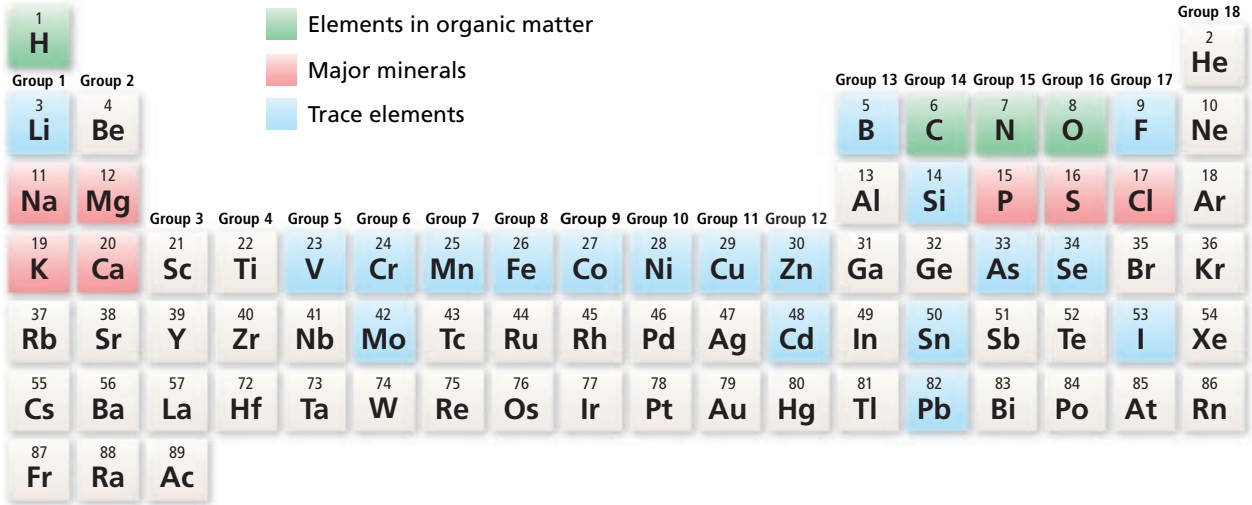


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TABLE 3C Transition Metal Trace Elements

Transition metal	Function
Vanadium, Cadmium	function not fully determined, but linked to a reduced growth rate and impaired reproduction
Chromium	needed for glucose transport to cells
Manganese	used in the enzyme reactions that synthesize cholesterol and metabolize carbohydrates
Iron	central atom in the heme molecule—a component of hemoglobin, which binds oxygen in the blood for transport to cells
Cobalt	a component of vitamin B_{12}
Nickel	enzyme cofactor in the metabolism of fatty acids and amino acids
Copper	a major component of an enzyme that functions to protect cells from damage
Zinc	needed for tissue growth and repair and as an enzyme cofactor
Molybdenum	enzyme cofactor in the production of uric acid

Role of Iron

Most iron in the body is in hemoglobin. Fe^{3+} is the central ion in the heme molecule, which is a component of the proteins hemoglobin and myoglobin. Hemoglobin in red blood cells transports oxygen to cells and picks up carbon dioxide as waste. Myoglobin is a protein that stores oxygen to be used in muscle contraction. Iron is also in the proteins of the electron transport system and the immune system.

Mechanisms of the body control the rate of iron absorption from food in the diet. When iron reserves are low, chemical signals stimulate cells of the intestines to absorb more iron during digestion. If the diet is low in iron, causing a deficiency, hemoglobin production stops and a condition called iron-deficiency anemia results. The blood cells produced during this state are stunted and unable to deliver adequate oxygen to cells. As a result, a person with iron-deficiency anemia feels tired and weak and has difficulty maintaining normal body temperature. The recommended daily intake of iron is 15 mg. The recommended level doubles for pregnant women. Iron supplements are for people who do not get enough iron in their daily diets. Table 3D lists some foods that are good sources of iron in the diet. Too much iron can be toxic because the body stores iron once it is absorbed. Abusing iron supplements can cause severe liver and heart damage.

TABLE 3D Sources of Iron in Foods

Food	Serving size	Iron present (mg)
Beef roast (lean cut)	4 oz	3.55
Beef, T-bone steak (lean cut)	4 oz	3.40
Beef, ground (hamburger)	4 oz	2.78
Broccoli	6.3 oz	1.50
Chicken, breast	4 oz	1.35
Chicken, giblets	4 oz	7.30
Oatmeal, instant enriched	1 pkg	8.35
Pita bread, white enriched	6 1/2 in. diameter	1.40
Pork roast	4 oz	1.15
Prunes	4 oz	2.00
Raisins	4 oz	1.88

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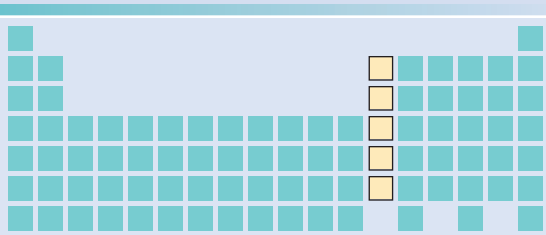
GROUP 13
BORON FAMILY



CHARACTERISTICS

- do not occur naturally in element form
- are scarce in nature (except aluminum, which is the most abundant metallic element)
- consist of atoms that have three electrons in their outer energy level
- are metallic solids (except boron, which is a solid metalloid)
- are soft and have low melting points (except boron, which is hard and has a high melting point)
- are chemically reactive at moderate temperatures (except boron)

5
B
Boron
10.811
$[He]2s^2 2p^1$

13
Al
Aluminum
26.981539
$[Ne]3s^2 3p^1$

31
Ga
Gallium
69.723
$[Ar]3d^{10} 4s^2 4p^1$

49
In
Indium
114.818
$[Kr]4d^{10} 5s^2 5p^1$

81
Tl
Thallium
204.3833
$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$

Atomic radius increases

Ionic radius increases

Ionization energy decreases

Boron is a covalent solid. Other members of the family are metallic solids.

The warmth of a person's hand will melt gallium. Gallium metal has the lowest melting point (29.77°C) of any metal except mercury.

Aluminum is the most abundant metal in Earth's crust. It exists in nature as an ore called bauxite.

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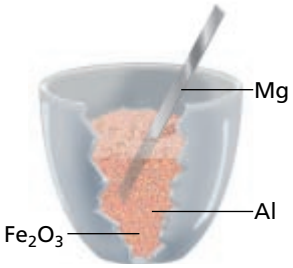
COMMON REACTIONS

The reaction chemistry of boron differs greatly from that of the other members of this family. Pure boron is a covalent network solid, whereas the other members of the family are metallic crystals in pure form. Boron resembles silicon more closely than it resembles the other members of its family.



A mixture of powdered aluminum and iron(III) oxide is called thermite. Al reacts with Fe_2O_3 using Mg ribbon as a fuse to provide activation energy. The energy produced by the thermite reaction is sufficient to produce molten iron as a product.

With Strong Bases to Form Hydrogen Gas and a Salt

Example: $2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow 2NaAlO_2(aq) + 3H_2(g)$

Ga also follows this pattern.

With Dilute Acids to Form Hydrogen Gas and a Salt

Example: $2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$

Ga, In, and Tl follow this pattern in reacting with dilute HF, HCl, HBr, and HI.

Example: $Al(s) + 4HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + NO(g) + 2H_2O(l)$

With Halogens to Form Halides

Example: $2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$

B, Al, Ga, In, and Tl also follow this pattern in reacting with F_2, Cl_2, Br_2, and I_2 (except BF_3).

With Oxygen to Form Oxides

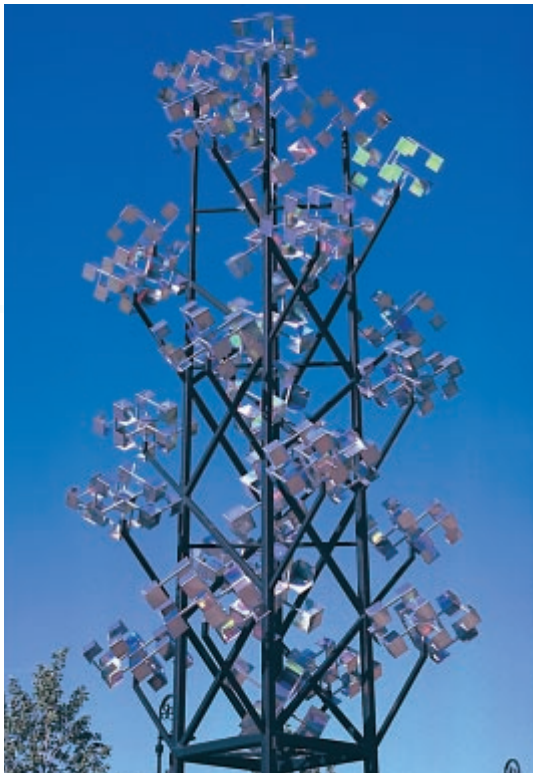
Example: $4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$

Ga, In, and Tl also follow this pattern.

ANALYTICAL TEST

Other than atomic absorption spectroscopy, there is no simple analytical test for all the members of the boron family.

The confirmatory test for the presence of aluminum in qualitative analysis is the formation of $Al(OH)_3$, which may be hard to detect in solution. The precipitate is made visible by the addition of a red dye called aluminum reagent.



Aluminum forms a thin layer of Al_2O_3, which protects the metal from oxidation and makes it suitable for outdoor use.

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PROPERTIES OF THE GROUP 13 ELEMENTS

	B	Al	Ga	In	Tl
Melting point (°C)	2300	660.37	29.77	156.61	303.5
Boiling point (°C)	2550	2467	2203	2080	1457
Density (g/cm^3)	2.34	2.702	5.904	7.31	11.85
Ionization energy (kJ/mol)	801	578	579	558	589
Atomic radius (pm)	85	143	135	167	170
Ionic radius (pm)	—	54	62	80	89
Common oxidation number in compounds	+3	+3	+1, +3	+1, +3	+1, +3
Crystal structure	monoclinic	fcc	orthorhombic	fcc	hcp
Hardness (Mohs' scale)	9.3	2.75	1.5	1.2	1.2

APPLICATION *Technology*

Aluminum

Chemically, aluminum is much more active than copper, and it belongs to the category of *self-protecting metals*. These metals are oxidized when exposed to oxygen in the air and form a hard, protective metal oxide on the surface. The oxidation of aluminum is shown by the following reaction.

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

This oxide coating protects the underlying metal from further reaction with oxygen or other substances. Self-protecting metals are valuable in themselves or when used to coat iron and steel to keep them from corroding.

Aluminum is a very good conductor of electric current. Many years ago, most high-voltage electric power lines were made of copper. Although copper is a better conductor of electricity than aluminum, copper is heavier and more expensive. Today more than 90% of high-voltage transmission lines are made of relatively pure aluminum. The aluminum wire does not have to be self-supporting because steel cable is incorporated to bear the weight of the wire in the long spans between towers.

In the 1960s, aluminum electric wiring was used in many houses and other buildings. Over time, however, because the aluminum oxidized, Al_2O_3 built up and increased electric resistance at points where wires connected to outlets, switches, and other metals. As current flowed through the extra resistance, enough heat was generated to cause a fire. Though some homes have been rewired, aluminum wiring is still prevalent in many homes.

These high-voltage transmission lines are made of aluminum supported with steel cables.

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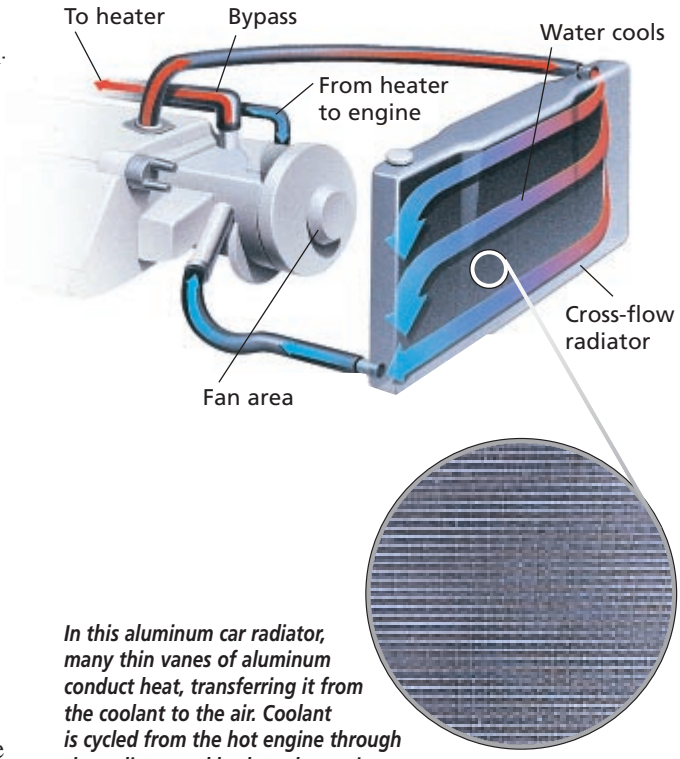
Aluminum Alloys

Because aluminum has a low density and is inexpensive, it is used to construct aircraft, boats, sports equipment, and other lightweight, high-strength objects. The pure metal is not strong, so it is mixed with small quantities of other metals—usually manganese, copper, magnesium, zinc, or silicon—to produce strong low-density alloys. Typically, 80% of a modern aircraft frame consists of aluminum alloy.

Aluminum and its alloys are good conductors of heat. An alloy of aluminum and manganese is used to make cookware. High-quality pots and pans made of stainless steel may have a plate of aluminum on the bottom to help conduct heat quickly to the interior.

Automobile radiators made of aluminum conduct heat as hot coolant from the engine enters the bottom of the radiator. The coolant is deflected into several channels. These channels are covered by thin vanes of aluminum, which conduct heat away from the coolant and transfer it to the cooler air rushing past. By the time the coolant reaches the top of the radiator, its temperature has dropped so that when it flows back into the engine it can absorb more heat. To keep the process efficient, the outside of a radiator should be kept unobstructed and free of dirt buildup.



In this aluminum car radiator, many thin vanes of aluminum conduct heat, transferring it from the coolant to the air. Coolant is cycled from the hot engine through the radiator and back to the engine.

TABLE 4A Alloys of Aluminum and Their Uses

Principal alloying element(s)*	Characteristics	Application examples
Manganese	moderately strong, easily worked	cookware, roofing, storage tanks, lawn furniture
Copper	strong, easily formed	aircraft structural parts; large, thin structural panels
Magnesium	strong, resists corrosion, easy to weld	parts for boats and ships, outdoor decorative objects, tall poles
Zinc and magnesium	very strong, resists corrosion	aircraft structural parts, vehicle parts, anything that needs high strength and low weight
Silicon	expands little on heating and cooling	aluminum castings
Magnesium and silicon	resists corrosion, easily formed	exposed parts of buildings, bridges

* All these alloys have small amounts of other elements.

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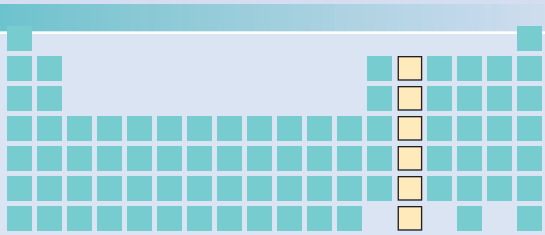
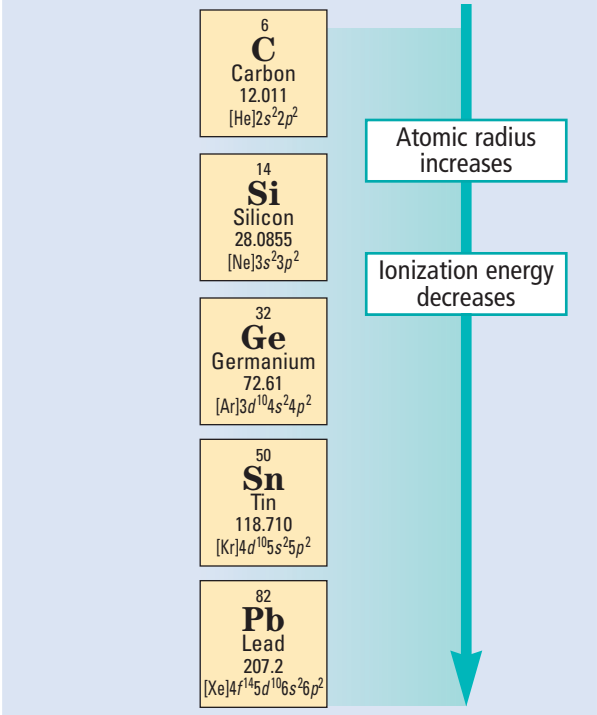
GROUP 14
CARBON FAMILY



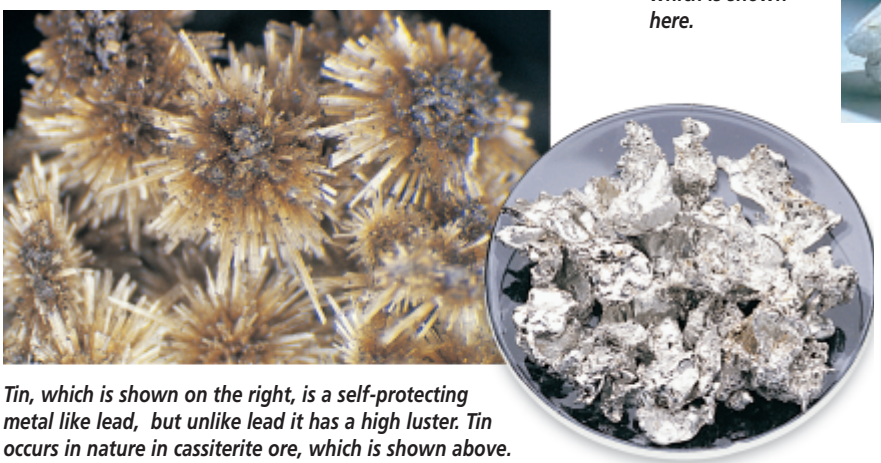
CHARACTERISTICS

- include a nonmetal (carbon), two metalloids (silicon and germanium), and two metals (tin and lead)
- vary greatly in both physical and chemical properties
- occur in nature in both combined and elemental forms
- consist of atoms that contain four electrons in the outermost energy level
- are relatively unreactive
- tend to form covalent compounds (tin and lead also form ionic compounds)



Lead has a low reactivity and is resistant to corrosion. It is very soft, highly ductile, and malleable. Lead is toxic and, like mercury, it is a cumulative poison.

Silicon has a luster but does not exhibit metallic properties. Most silicon in nature is a silicon oxide, which occurs in sand and quartz, which is shown here.



Tin, which is shown on the right, is a self-protecting metal like lead, but unlike lead it has a high luster. Tin occurs in nature in cassiterite ore, which is shown above.

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COMMON REACTIONS

With Oxygen to Form Oxides

Example: $Sn(s) + O_2(g) \longrightarrow SnO_2(s)$

Pb follows this pattern, as do C, Si, and Ge at high temperatures.

With Acids to Form Salts and Hydrogen Gas

Only the metallic elements of this group react slowly with aqueous acids.

Example: $Sn(s) + 2HCl(aq) \longrightarrow SnCl_2(aq) + H_2(g)$

Both Sn and Pb can also react to form tin(IV) and lead(IV) salts, respectively.

With Halogens to Form Halides

Example: $Sn(s) + 2Cl_2(g) \longrightarrow SnCl_4(s)$

Si, Ge, and Pb follow this pattern, reacting with F_2, Cl_2, Br_2, and I_2.

ANALYTICAL TEST

The only way to identify all the elements of this group is by atomic absorption spectroscopy. Ionic compounds of tin and lead can be identified in aqueous solutions by adding a solution containing sulfide ions. The formation of a yellow precipitate indicates the presence of Sn^{4+}, and the formation of a black precipitate indicates the presence of Pb^{2+}.

$$Sn^{4+}(aq) + 2S^{2-}(aq) \longrightarrow SnS_2(s)$$
$$Pb^{2+}(aq) + S^{2-}(aq) \longrightarrow PbS(s)$$

PbS

SnS_2

PROPERTIES OF THE GROUP 14 ELEMENTS

	C	Si	Ge	Sn	Pb
Melting point (°C)	3500/3652*	1410	937.4	231.88	327.502
Boiling point (°C)	3930	2355	2830	2260	1740
Density (g/cm^3)	3.51/2.25*	2.33 ± 0.01	5.323	7.28	11.343
Ionization energy (kJ/mol)	1086	787	762	709	716
Atomic radius (pm)	77	118	122	140	175
Ionic radius (pm)	260 (C^{4-} ion)	—	—	118 (Sn^{2+} ion)	119 (Pb^{2+} ion)
Common oxidation number in compounds	+4, –4	+4	+2, +4	+2, +4	+2, +4
Crystal structure	cubic/hexagonal*	cubic	cubic	tetragonal	fcc
Hardness (Mohs' scale)	10/0.5*	6.5	6.0	1.5	1.5

* The data are for two allotropic forms: diamond/graphite.

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APPLICATION *Chemical Industry*

Carbon and the Reduction of Iron Ore

Some metals, especially iron, are separated from their ores through reduction reactions in a blast furnace. The blast furnace gets its name from the fact that air or pure oxygen is blown into the furnace, where it oxidizes carbon to form carbon monoxide, CO. Carbon and its compounds are important reactants in this process.

What happens inside the blast furnace to recover the iron from its ore? The actual chemical changes that occur are complex. A simplified explanation begins with the reaction of oxygen in hot air with coke, a form of carbon. Some of the coke burns to form carbon dioxide.

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

As the concentration of oxygen is increased, the carbon dioxide comes in contact with pieces of hot coke and is reduced to carbon monoxide.

$$CO_2(g) + C(s) \longrightarrow 2CO(g)$$

The carbon monoxide now acts as a reducing agent to reduce the iron oxides in the ore to metallic iron.

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(l) + 3CO_2(g)$$

The reduction is thought to occur in steps as the temperature in the furnace increases. The following are some of the possible steps.

$$Fe_2O_3 \longrightarrow Fe_3O_4 \longrightarrow FeO \longrightarrow Fe$$

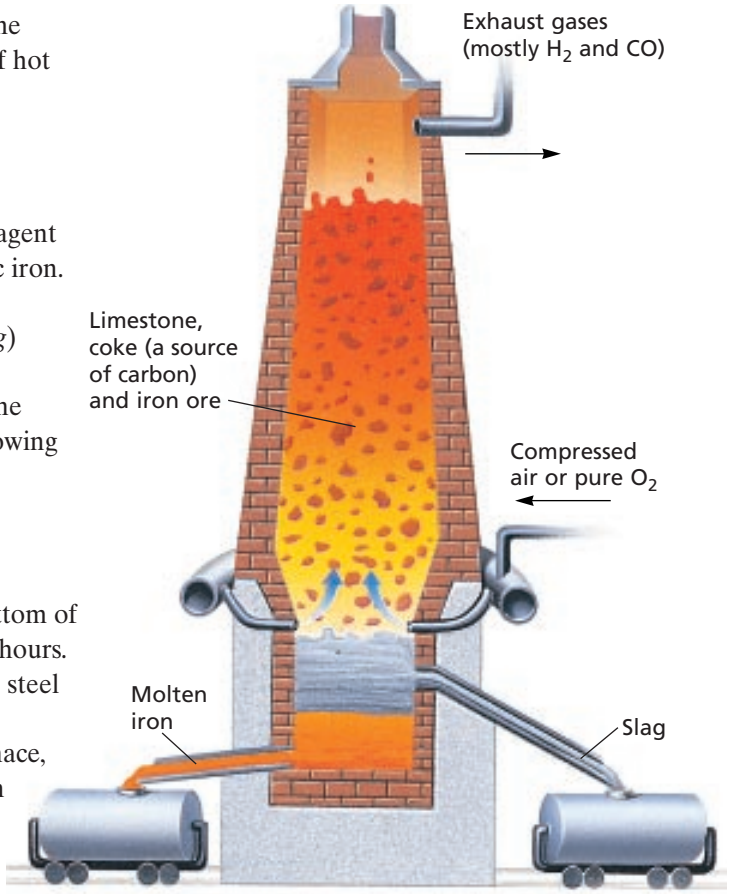
The white-hot liquid iron collects in the bottom of the furnace and is removed every four or five hours. The iron may be cast in molds or converted to steel in another process.

Limestone, present in the center of the furnace, decomposes to form calcium oxide and carbon dioxide.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The calcium oxide then combines with silica, a silicon compound, to form calcium silicate slag.

The relatively high carbon content of iron produced in a blast furnace makes the metal hard but brittle. It also has other impurities, like sulfur and phosphorus, that cause the recovered iron to be brittle. The conversion of iron to steel is essentially a purification process in which impurities are removed by oxidation. This purification process is carried out in another kind of furnace at very high temperatures. All steel contains 0.02 to 1.5% carbon. In fact, steels are graded by their carbon content. Low-carbon steels typically contain 0.02 to 0.3% carbon. Medium-carbon steels typically contain 0.03 to 0.7% carbon. High-carbon steels contain 0.7 to 1.5% carbon.



Molten iron flowing from the bottom of a blast furnace has been reduced from its ore through a series of reactions at high temperatures in different regions of the furnace.

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Carbon Dioxide

Carbon dioxide is a colorless gas with a faintly irritating odor and a slightly sour taste. The sour taste is the result of the formation of carbonic acid when CO_2 dissolves in the water in saliva. It is a stable gas that does not burn or support combustion. At temperatures lower than 31°C and at pressures higher than 72.9 atm, CO_2 condenses to the liquid form. A phase diagram for CO_2 is found in the chapter review section of Chapter 12. At normal atmospheric pressure, solid CO_2 (dry ice) sublimes at –78.5°C. The linear arrangement of carbon dioxide molecules makes them nonpolar.

CO_2 is produced by the burning of organic fuels and from respiration processes in most living things. Most CO_2 released into the atmosphere is used by plants during photosynthesis. Recall that photosynthesis is the process by which green plants and some forms of algae and bacteria make food. During photosynthesis, CO_2 reacts with H_2O, using the energy from sunlight. The relationships among the various processes on Earth that convert carbon to carbon dioxide are summarized in the diagram of the carbon cycle, which is pictured below.

Carbon Monoxide

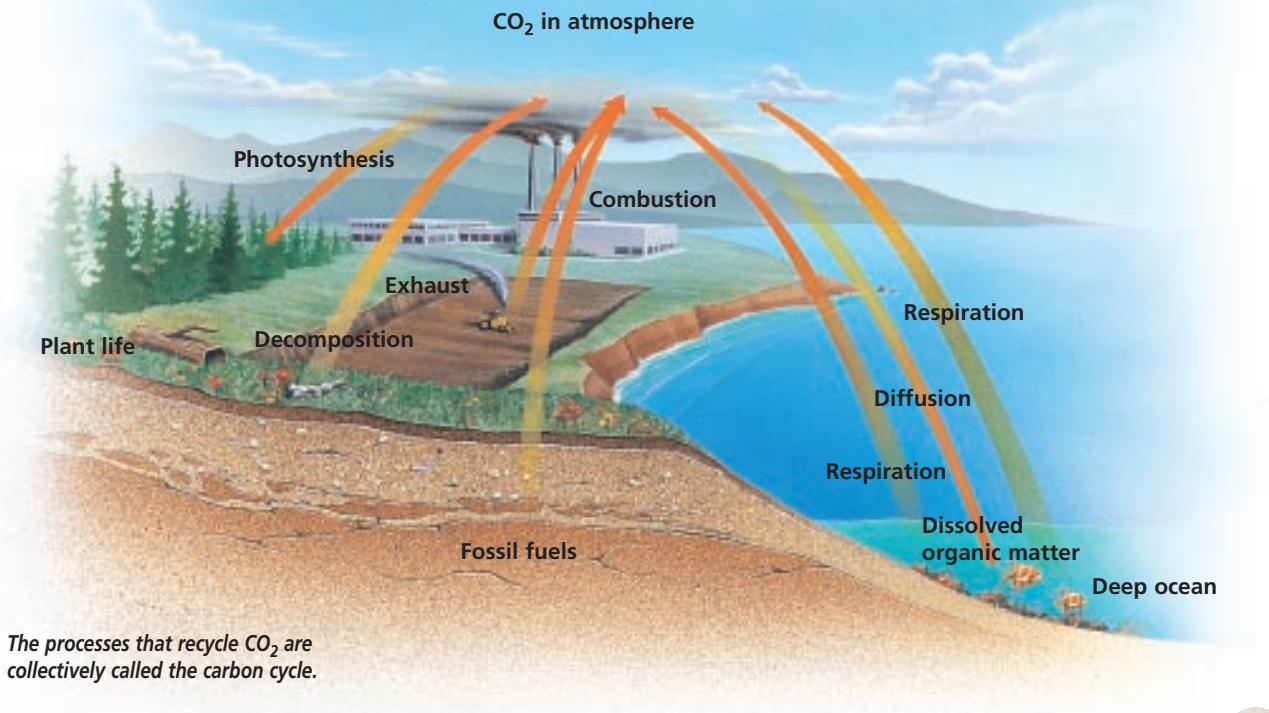
Carbon monoxide is a poisonous gas produced naturally by decaying plants, certain types of algae, volcanic eruptions, and the oxidation of methane in the atmosphere.

Because CO is colorless, odorless, and tasteless, it is difficult to detect. It is slightly less dense than air and slightly soluble in water. Its main chemical uses are in the reduction of iron, described on page 756, and the production of organic compounds, such as methanol.

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

Carbon monoxide is also produced during the incomplete combustion of organic fuels. Incomplete combustion of methane occurs when the supply of oxygen is limited.

$$2CH_4(g) + 3O_2(g) \longrightarrow 2CO(g) + 4H_2O(g)$$



The processes that recycle CO_2 are collectively called the carbon cycle.

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APPLICATION *Biochemistry*

Carbon Dioxide and Respiration

Many organisms, including humans, carry out cellular respiration. In this process, cells break down food molecules and release the energy used to build those molecules during photosynthesis. Glucose, $C_6H_{12}O_6$, is a common substance broken down in respiration. The following chemical equation expresses this process.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

In humans and most other vertebrate animals, the oxygen needed for this reaction is delivered to cells by hemoglobin found in red blood cells. Oxygen binds with hemoglobin as blood passes through capillaries in the lungs, as represented by the following reaction.

$$Hb + O_2 \longrightarrow HbO_2$$

Hb represents the hemoglobin molecule, and HbO_2 represents oxyhemoglobin, which is hemoglobin with bound oxygen. When the red blood cells pass through capillaries near cells that have depleted their oxygen supply through respiration, the reaction reverses and oxyhemoglobin gives up its oxygen.

$$HbO_2 \longrightarrow Hb + O_2$$

Carbon dioxide produced during respiration is a waste product that must be expelled from an organism. Various things happen when CO_2 enters the blood. Seven percent dissolves in the plasma, about 23% binds loosely to hemoglobin, and the remaining 70% reacts reversibly with water in plasma to form hydrogen carbonate, HCO_3^- ions. To form HCO_3^- ions, CO_2 first combines with H_2O to form carbonic acid, H_2CO_3, in a reversible reaction.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

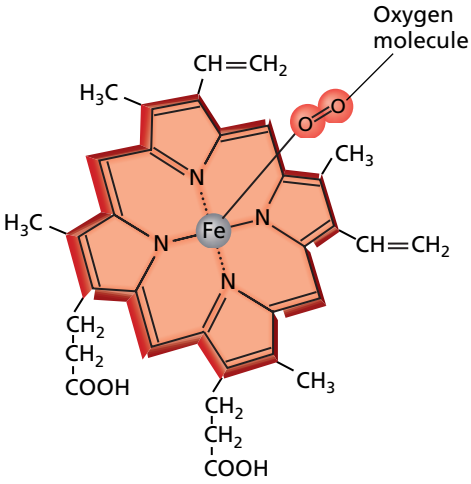
The dissolved carbonic acid ionizes to HCO_3^- ions and aqueous H^+ ions in the form of H_3O^+.

$$H_2CO_3(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

The combined equilibrium reaction follows.

$$CO_2(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

When the blood reaches the lungs, the reaction reverses and the blood releases CO_2, which is then exhaled to the surroundings.



Heme

Hemoglobin (protein)

Red blood cells

The oxygen carrier molecule, heme, is a component of the more-complex protein hemoglobin. Note that each hemoglobin molecule has four heme subunits. Hemoglobin is a component of red blood cells.

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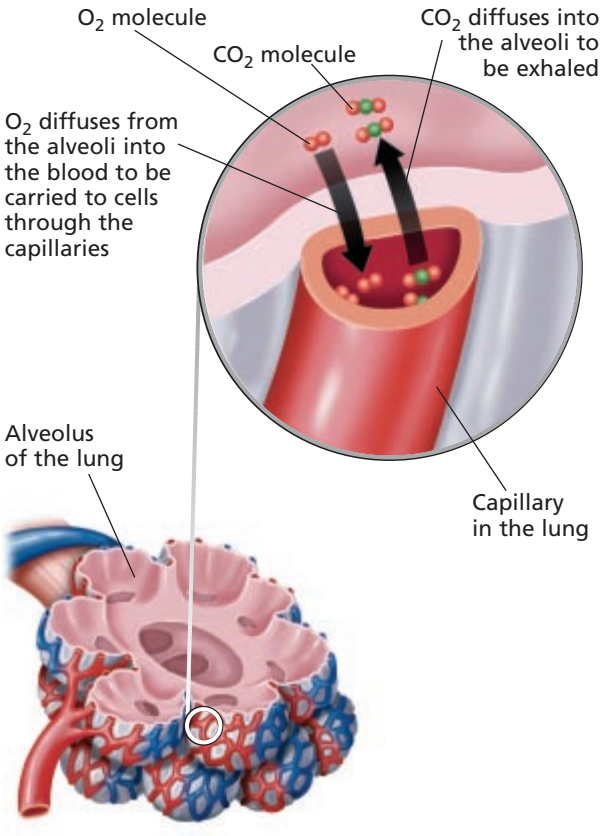
Exchange of CO_2 and O_2 in the Lungs

Why does CO_2 leave the blood as it passes through the lung's capillaries, and why does O_2 enter the blood? The exchange is caused by the difference in concentrations of CO_2 and O_2 in the blood and in the atmosphere. Oxygen is 21% of the atmosphere. Although the amount of CO_2 varies from place to place, it averages about 0.033% of the atmosphere. Thus, O_2 is about 640 times more concentrated in the atmosphere than is CO_2.

Substances tend to diffuse from regions of higher concentration toward regions of lower concentration. Thus, when blood reaches the capillaries of the lung, O_2 from the air diffuses into the blood, where its pressure is only 40 mm Hg, while CO_2 diffuses out of the blood, where its pressure is 45 mm Hg, and into the air. The diagram below summarizes the process.


O_2 molecule
CO_2 molecule
CO_2 diffuses into the alveoli to be exhaled
O_2 diffuses from the alveoli into the blood to be carried to cells through the capillaries
Alveolus of the lung
Capillary in the lung

The pressure of O_2 in the blood entering the lung is much lower than it is in the atmosphere. As a result, O_2 diffuses into the blood. The opposite situation exists for CO_2, so it diffuses from the blood into the air. Note that blood leaving the lung still contains a significant concentration of CO_2.

Acidosis and Alkalosis

In humans, blood is maintained between pH 7.3 and 7.5. The pH of blood is dependent on the concentration of CO_2 in the blood. Look again at this equilibrium system.

$$CO_2(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

Notice that the right side of the equation contains the H_3O^+ ion, which determines the pH of the blood. If excess H_3O^+ enters the blood from tissues, the reverse reaction is favored. Excess H_3O^+ combines with HCO_3^- to produce more CO_2 and H_2O. If the H_3O^+ concentration begins to fall, the forward reaction is favored, producing additional H_3O^+ and HCO_3^-. To keep H_3O^+ in balance, adequate amounts of both CO_2 and HCO_3^- must be present. If something occurs that changes these conditions, a person can become very ill and can even die.

Hyperventilation occurs when a person breathes too rapidly for an extended time. Too much CO_2 is eliminated, causing the reverse reaction to be favored, and H_3O^+ and HCO_3^- are used up. As a result, the person develops a condition known as alkalosis because the pH of the blood rises to an abnormal alkaline level. The person begins to feel lightheaded and faint, and, unless treatment is provided, he or she may fall into a coma. Alkalosis is treated by having the victim breathe air that is rich in CO_2. One way to accomplish this is to have the person breathe with a bag held tightly over the nose and mouth. Alkalosis is also caused by fever, infection, intoxication, hysteria, and prolonged vomiting.

The reverse of alkalosis is a condition known as acidosis. This condition is often caused by a depletion of HCO_3^- ions from the blood, which can occur as a result of kidney dysfunction. The kidney controls the excretion of HCO_3^- ions. If there are too few HCO_3^- ions in solution, the forward reaction is favored and H_3O^+ ions accumulate, which lowers the blood's pH. Acidosis can also result from the body's inability to expel CO_2, which can occur during pneumonia, emphysema, and other respiratory disorders. Perhaps the single most common cause of acidosis is uncontrolled diabetes, in which acids normally excreted in the urinary system are instead retained by the body.

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APPLICATION *The Environment*

Carbon Monoxide Poisoning

Standing on a street corner in any major city exposes a person to above-normal concentrations of carbon monoxide from automobile exhaust. Carbon monoxide also reacts with hemoglobin. The following reaction takes place in the capillaries of the lung.

$$Hb + CO \longrightarrow HbCO$$

Unlike CO_2 or O_2, CO binds strongly to hemoglobin. Carboxyhemoglobin, HbCO, is 200 times more stable than oxyhemoglobin, HbO_2. So as blood circulates, more and more CO molecules bind to hemoglobin, reducing the amount of O_2 bond sites available for transport. Eventually, CO occupies so many hemoglobin binding sites that cells die from lack of oxygen. Symptoms of carbon monoxide poisoning include headache, mental confusion, dizziness, weakness, nausea, loss of muscular control, and decreased heart rate and respiratory rate. The victim loses consciousness and will die without treatment.

If the condition is caught in time, a victim of carbon monoxide poisoning can be revived by breathing pure oxygen. This treatment causes carboxyhemoglobin to be converted slowly to oxyhemoglobin according to the following chemical equation.

$$O_2 + HbCO \longrightarrow CO + HbO_2$$

Mild carbon monoxide poisoning usually does not have long-term effects. In severe cases, cells are destroyed. Damage to brain cells is irreversible.

The level of danger posed by carbon monoxide depends on two factors: the concentration of the gas in the air and the amount of time that a person is exposed to the gas. Table 5A shows the effects of increasing levels of carbon monoxide in the bloodstream. These effects vary considerably depending on a person's activity level and metabolic rate.

Carbon monoxide detectors are now available to reduce the risk of poisoning from defective home heating systems. The Consumer Products Safety Commission recommends that all homes have a CO detector with a UL label.

TABLE 5A Symptoms of CO Poisoning at Increasing Levels of CO Exposure and Concentration

Concentration of CO in air (ppm)*	Hemoglobin molecules as HbCO	Visible effects
100 for 1 hour or less	10% or less	no visible symptoms
500 for 1 hour or less	20%	mild to throbbing headache, some dizziness, impaired perception
500 for an extended period of time	30–50%	headache, confusion, nausea, dizziness, muscular weakness, fainting
1000 for 1 hour or less	50–80%	coma, convulsions, respiratory failure, death

* ppm is parts per million

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APPLICATION *Biochemistry*

Macromolecules

Large organic polymers are called macromolecules (the prefix *macro* means "large"). Macromolecules play important roles in living systems. Most macromolecules essential to life belong to four main classes, three of which we know as nutrients in food:

1. **Proteins** Hair, tendons, ligaments, and silk are made of protein. Other proteins act as hormones, transport substances throughout the body, and fight infections. Enzymes are proteins that control the body's chemical reactions. Proteins provide energy, yielding 17 kJ/g.
2. **Carbohydrates** Sugars, starches, and cellulose are carbohydrates. Carbohydrates are sources of energy, yielding 17 kJ/g.
3. **Lipids** Fats, oils, waxes, and steroids are lipids, nonpolar substances that do not dissolve in water. Fats are sources of energy, yielding 38 kJ/g.
4. **Nucleic acids** The nucleic acids are DNA and RNA. In most organisms, DNA is used to store hereditary information and RNA helps to assemble proteins.

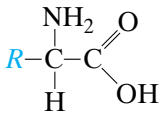
Proteins

Proteins are macromolecules formed by condensation reactions between amino acid monomers. Proteins contain carbon, oxygen, hydrogen, nitrogen, and usually some sulfur.

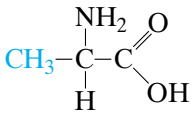
All amino acids have a carboxyl group, —COOH, and an amino group, —NH_2, attached to a central carbon atom, which is also attached to hydrogen, —H. Amino acids differ from one another at the fourth bond site of the central carbon, which is attached to a group of atoms (called an *R* group). *R* groups differ from one amino acid to another, as shown in the structures for several amino acids below. The proteins of all organisms contain a set of 20 common amino acids. The reaction that links amino acids is a condensation reaction, which is described in Chapter 21.

Each protein has its own unique sequence of amino acids. A complex organism has at least several thousand different proteins, each with a special structure and function. For instance, *insulin,* a hormone that helps the body regulate the level of sugar in the blood, is made up of two linked chains.

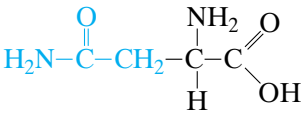
Amino acids have the same general structure. These examples show some of the variations within this class of compounds.



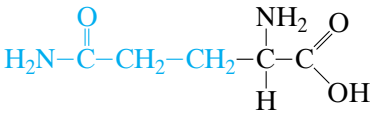
General structure



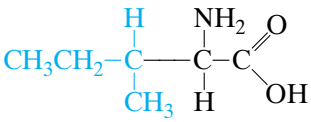
Alanine



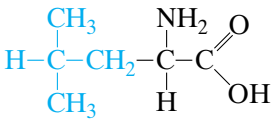
Asparagine



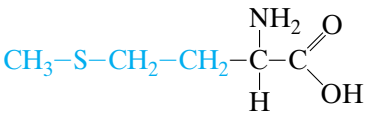
Glutamine



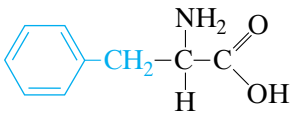
Isoleucine



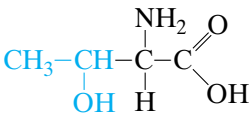
Leucine



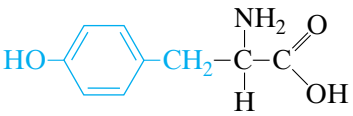
Methionine



Phenylalanine



Threonine



Tyrosine

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Hemoglobin is a complex protein made of hundreds of amino acids. Its 3-dimensional shape is called a tertiary structure. Tertiary structures break down when a protein is denatured.

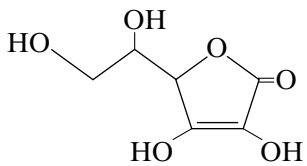
The chains are held together by S—S bonds between sulfur atoms in two cysteine amino acids. Insulin is one of the smaller proteins, containing only 51 amino acids. In contrast, hemoglobin, which carries oxygen in the blood, is a large protein consisting of four long chains with the complicated three-dimensional structures shown above. Proteins can lose their shape with increases in temperature or changes in the chemical composition of their environment. When they are returned to normal surroundings, they may fold or coil up again and re-form their original structure.

Changing even one amino acid can change a protein's structure and function. For example, the difference between normal hemoglobin and the hemoglobin that causes sickle cell anemia is just two amino acids.

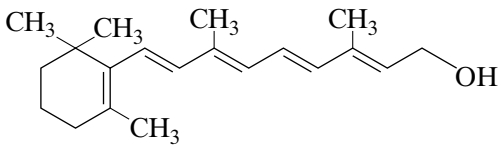
Enzymes

You learned how enzymes alter reaction rates in Chapter 17. Some enzymes cannot bind to their substrates without the help of additional molecules. These may be *minerals,* such as calcium or iron ions, or helper molecules called *coenzymes* that play accessory roles in enzyme-catalyzed reactions. Many vitamins are coenzymes or parts of coenzymes.

Vitamins are organic molecules that we cannot manufacture and hence need to eat in small amounts.



Vitamin C, $C_6H_8O_6$
Water-soluble



Vitamin A, $C_{20}H_{30}O$
Fat-soluble

You can see why we need vitamins and minerals in our diet—to enable our enzymes to work. You can also see why we need only small amounts of them. Minerals and coenzymes are not destroyed in biochemical reactions. Like enzymes, coenzymes and minerals can be used over and over again.

Temperature and pH have the most significant effects on the rates of reactions catalyzed by enzymes. Most enzymes work best in a solution of approximately neutral pH. Most body cells have a pH of 7.4. However, some enzymes function only in acidic or basic environments. For example, pepsin, the collective

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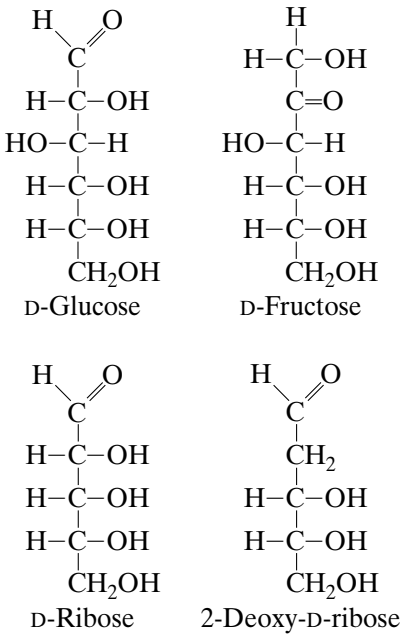
The protein in fish is denatured by the low pH of lime juice. Notice that the flesh shown with the limes has turned white compared with the flesh at normal pH.

term for the digestive enzymes found in the human stomach, works best at a very acidic pH of about 1.5. Cells that line the stomach secrete hydrochloric acid to produce this low pH environment. When food travels down the digestive tract, it carries these enzymes out of the stomach into the intestine. In the intestine, stomach enzymes stop working because sodium bicarbonate in the intestine raises the pH to about 8. Digestive enzymes in the intestine are formed by the pancreas and work best at pH 8.

Most chemical reactions, including enzyme reactions, speed up with increases in temperature. However, high temperatures (above about 60°C) destroy, or denature, protein by breaking up the three-dimensional structure. For example, the protein in an egg or a piece of meat denatures when the egg or meat is cooked. Proteins in the egg white become opaque when denatured. Heating can preserve food by denaturing the enzymes of organisms that cause decay. In milk pasteurization, the milk is heated to denature enzymes that would turn it sour. Refrigeration and freezing also help preserve food by slowing the enzyme reactions that cause decay.

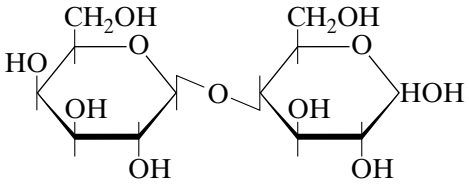
Carbohydrates

Carbohydrates are sugars, starches, and related compounds. The monomers of carbohydrates are monosaccharides, or simple sugars, such as fructose and glucose. A monosaccharide contains carbon, hydrogen, and oxygen in about a 1:2:1 ratio, which is an empirical formula of CH_2O.

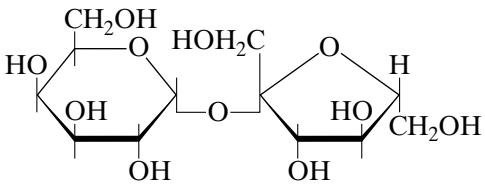


Monosaccharides chain representation

Two monosaccharides may be joined together to form a disaccharide. Sucrose, shown below, is a disaccharide. A disaccharide can be hydrolyzed to produce the monosaccharides that formed it. By a series of condensation reactions, many monosaccharides can be joined to form a polymer called a polysaccharide (commonly known as a complex carbohydrate).



Lactose—made from glucose and galactose



Sucrose—made from glucose and fructose

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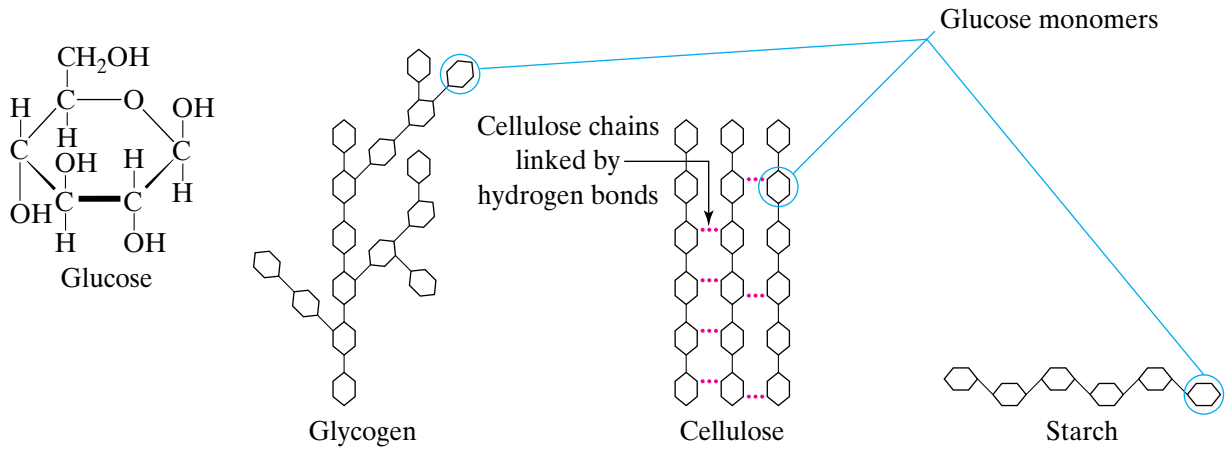


Glucose is the structural unit for glycogen, cellulose, and starch. Notice that these three polymers differ in the arrangement of glucose monomers.

Three important polysaccharides made of glucose monomers are glycogen, starch, and cellulose. Animals store energy in glycogen. The liver and muscles remove glucose from the blood and condense it into glycogen, which can later be hydrolyzed back into glucose and used to supply energy as needed.

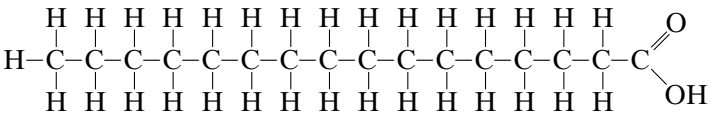
Starch consists of two kinds of glucose polymers. It is hydrolyzed in plants to form glucose for energy and for building material to produce more cells. The structural polysaccharide cellulose is probably the most common organic compound on Earth. Glucose monomers link cellulose chains together at the hydroxyl groups to form cellulose fibers. Cotton fibers consist almost entirely of cellulose.

Lipids

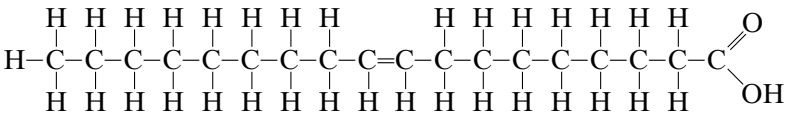
Lipids are a varied group of organic compounds that share one property: they are not very soluble in water. Lipids contain a high proportion of C—H bonds, and they dissolve in nonpolar organic solvents, such as ether, chloroform, and benzene.

Fatty acids are the simplest lipids. A fatty acid consists of an unbranched chain of carbon and hydrogen atoms with a carboxyl group at one end. Bonding within the carbon chain gives both saturated and unsaturated fatty acids, just as the simple hydrocarbons (see Chapter 20) can be saturated or unsaturated.

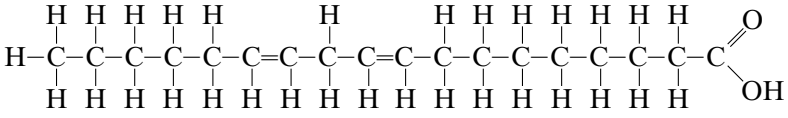
The bonds in a carboxyl group are polar, and so the carboxyl end of a fatty acid attracts water



Palmitic acid — saturated



Oleic acid — monounsaturated



Linoleic acid — polyunsaturated

These examples of common fatty acids show the differences in saturation level.

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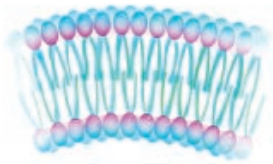
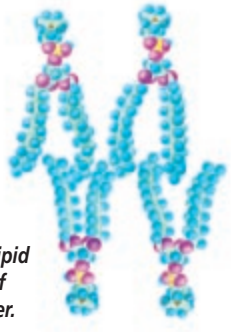
This phospholipid molecule contains two fatty-acid chains.

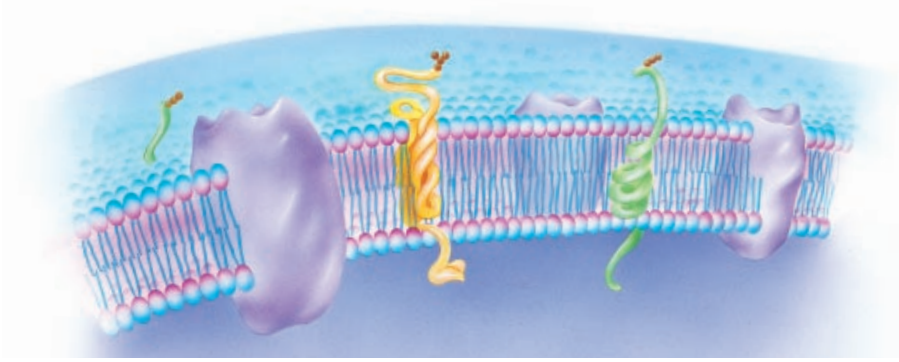


The lipid bilayer is the framework of the cell membrane.

The fatty acids are oriented toward the interior of the bilayer because they have a low attraction for water.



This phospholipid chain is part of the lipid bilayer.



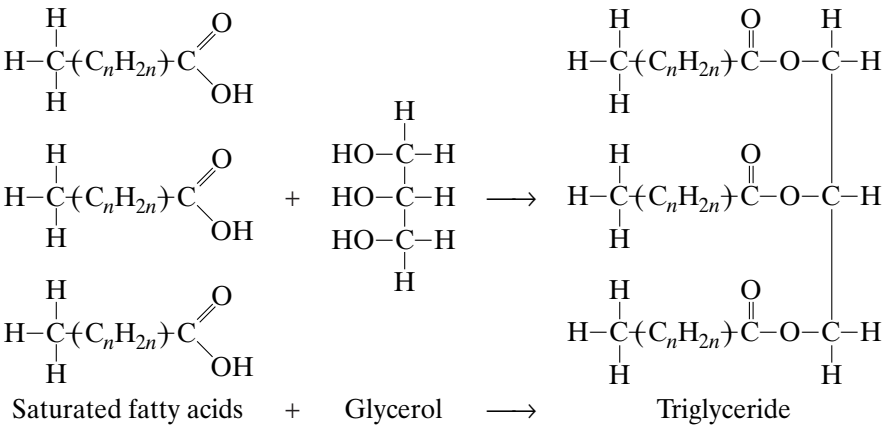
molecules. The carbon-hydrogen bonds of a lipid's hydrocarbon chain are nonpolar, however. The polar end will dissolve in water, and the other end will dissolve in nonpolar organic compounds. This behavior enables fatty acids to form membranes when they are dropped into water. It also gives soaps and detergents their cleaning power.

Lipids are the main compounds in biological membranes, such as the cell membrane. Because lipids are insoluble, the lipid bilayer of a cell membrane is adapted to keep the contents of the cell inside separated from the outer environment of the cell.

The structural component of a cell membrane is a phospholipid. The "head" of the phospholipid is polar, and the fatty acid tails are nonpolar, as shown in the model above.

Most fatty acids found in foods and soaps belong to a class of compounds called triglycerides. The fat content shown on a nutrition label for packaged food represents a mixture of the triglycerides in the food. Triglycerides have the general structure shown below.

Fatty acids are usually combined with other molecules to form classes of biomolecules called glycolipids (made from a carbohydrate and a lipid) or lipoproteins (made from a lipid and a protein). These compounds are also parts of more-complex lipids found in the body.



Triglycerides are made from three long-chain fatty acids bonded to a glycerol backbone.

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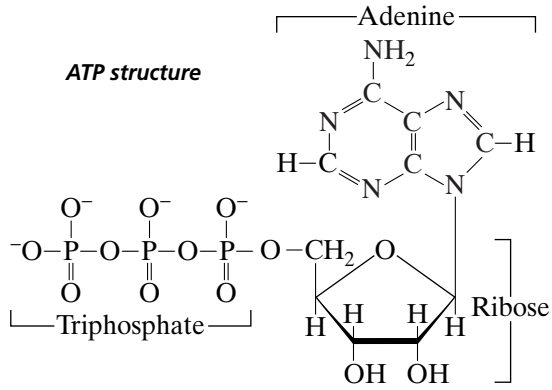
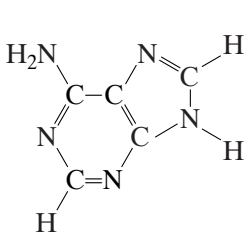
Nucleic Acids

Nucleic acids are macromolecules that transmit genetic information. Deoxyribonucleic acid (DNA) is the material that contains the genetic information that all organisms pass on to their offspring during reproduction. This information includes instructions for making proteins as well as for making the other nucleic acid, ribonucleic acid (RNA). Ribonucleic acid (RNA) assists in protein synthesis by helping to coordinate the process of protein assembly.

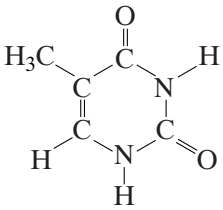
Nucleotides are the monomers of nucleic acids. A nucleotide has three parts: one or more phosphate groups, a sugar containing five carbon atoms, and a ring-shaped nitrogen base, as shown below. RNA nucleotides contain the simple sugar ribose. DNA nucleotides contain deoxyribose (ribose stripped of one oxygen atom). Structures for both of these sugars are shown on page 763. Cells contain nucleotides with one, two, or three phosphate groups attached. Besides being the monomers of nucleic acids, several nucleotides play other roles. For example, adenosine triphosphate (ATP) is the nucleotide that supplies the energy for many metabolic reactions.



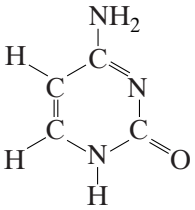
The bases in nucleic acids attract each other in pairs, a phenomenon known as base-pairing. DNA is made of four different nucleotides—those containing the bases adenine (A), thymine (T), guanine (G), and cytosine (C). The attraction between base pairs is hydrogen bonding. Adenine forms hydrogen bonds with thymine. Similarly, cytosine bonds to guanine. This base-pairing holds strands of DNA together.



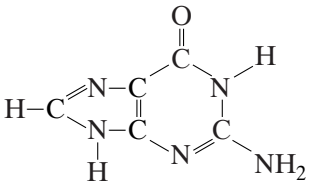
Adenine



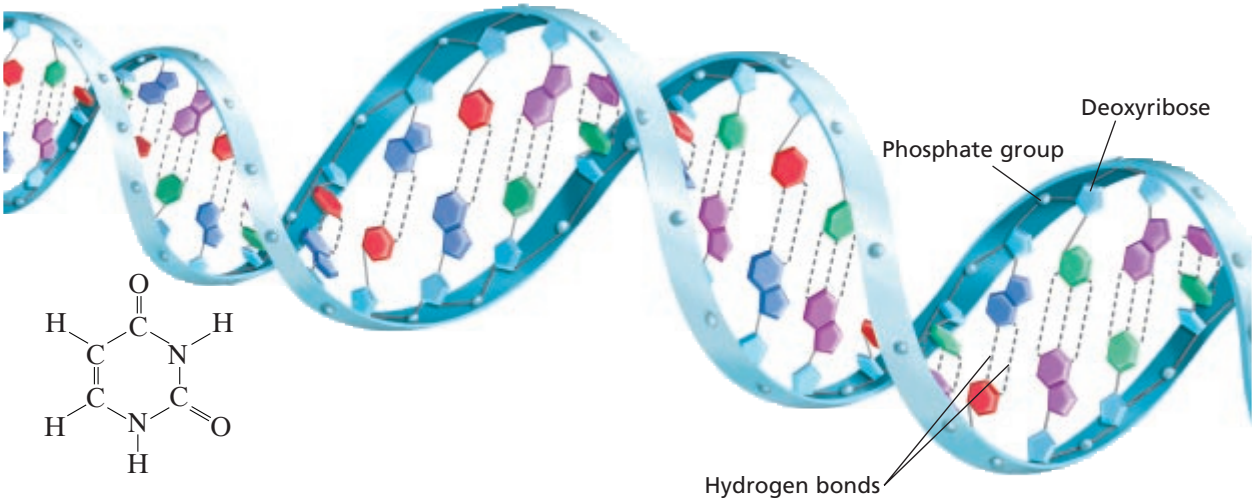
Thymine



Cytosine



Guanine



Uracil, RNA only

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APPLICATION *Chemical Industry*

Silicon and Silicates

Silicon is as important in the mineral world as carbon is in living systems. Silicon dioxide and silicates make up about 87% of the Earth's crust. Silicates are a class of compounds containing silicon, oxygen, one or more metals, and possibly hydrogen. Many mineral compounds are silicates. Sand is probably the most familiar silicate.

Glasses consist of 75% silicate. Borosilicate glass is the special heat-resistant glass used in making laboratory beakers and flasks. The addition of 5% boron oxide to the glass increases the softening temperature of the glass. Because boron and silicon atoms have roughly similar radii, these atoms can be substituted for one another to make borosilicate glass.

Asbestos is the name given to a class of fibrous magnesium silicate minerals. Asbestos is very strong and flexible, and it does not burn, so it was widely used as a heat-insulating material.

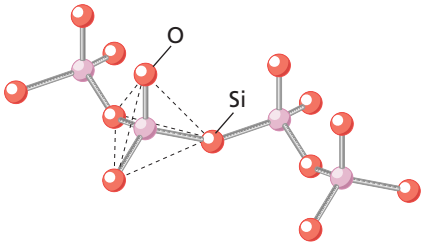
It is now known that asbestos is a carcinogen. When handled, asbestos releases dust particles that are easily inhaled and can cause lung cancer. Asbestos materials found in older homes and buildings should be removed by firms licensed by the Environmental Protection Agency (EPA).

Silicones

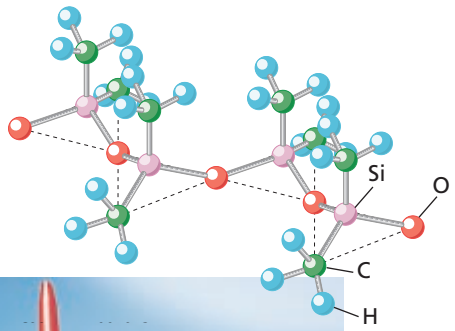
Silicones are a class of organic silicon polymers composed of silicon, carbon, oxygen, and hydrogen. The silicon chain is held together by bonding with the oxygen atoms. Each silicon atom is also bonded to different hydrocarbon groups to create a variety of silicone structures.

Silicones are widely used for their adhesive and protective properties. They have good electric insulating properties and are water-repellent. Some silicones have the character of oils or greases, so they are used as lubricants. Silicones are also used in automobile and furniture polishes as protective agents.

Silicon has the ability to form long chain compounds by bonding with oxygen. The SiO_4 subunit in this silicate is tetrahedral.



Silicones also have a tetrahedral structure. How does this structure differ from that of a silicate?



Silicates exist in a variety of mineral forms, including mica.

Because of their protective properties, silicones are used in a number of consumer products, from cosmetics to caulkings.

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APPLICATION *Technology*

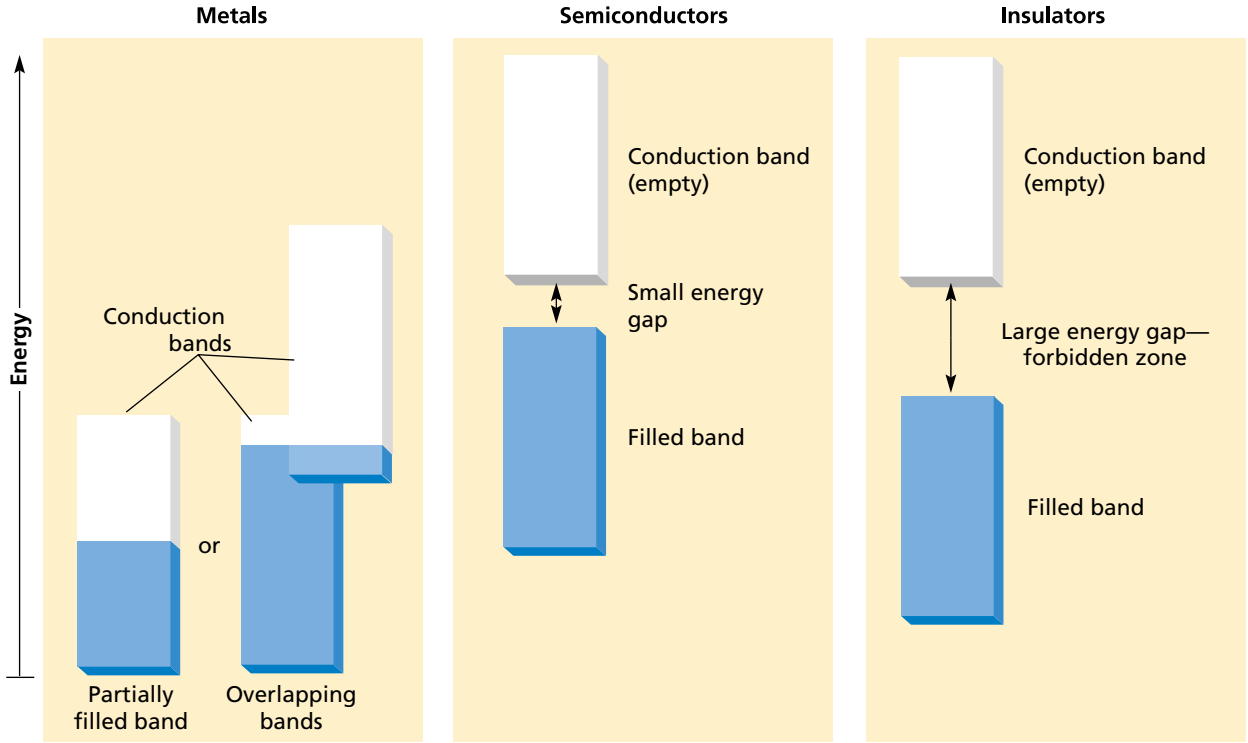
Semiconductors

When electrons can move freely through a material, the material is a conductor. The electrons in metals are loosely held and require little additional energy to move from one vacant orbital to the next. A set of overlapping orbitals is called a *conduction band*. Because electrons can easily jump to the conduction band, metals conduct electricity when only a very small voltage is applied.

Semiconductors conduct a current if the voltage applied is large enough to excite the outer-level electrons of their atoms into the higher energy levels. With semiconductors, more energy, and thus a higher voltage, is required to cause conduction. By contrast, nonmetals are insulators because they do not conduct at ordinary voltages. Too much energy is needed to raise their outer electrons into conduction bands.

Semiconductor devices include transistors; diodes, including light-emitting diodes (LEDs); some lasers; and photovoltaic cells ("solar" cells). Though silicon is the basis of most semiconductor devices in the computer industry, pure silicon has little use as a semiconductor. Instead, small amounts of impurities are added to increase its conductive properties. Adding impurities to silicon is called *doping,* and the substances added are *dopants.* The dopant is usually incorporated into just the surface layer of a silicon chip. Typical dopants include the Group 15 elements phosphorus and arsenic and the Group 13 elements boron, aluminum, gallium, and indium.

A silicon atom has four electrons in its outer energy level whereas Group 13 atoms have three and Group 15 atoms have five. Adding boron to silicon creates a mix of atoms having four valence electrons and atoms having three valence electrons. Boron atoms form only three bonds with silicon, whereas silicon forms four bonds with other silicon atoms. The unbonded spot between a silicon atom



This model shows the difference in the levels of energy required to excite electrons into the conduction band in metals, semiconductors, and insulators. The forbidden zone is too great an energy gap in insulators for these elements to function as conductors. The energy gap for semiconductors is small enough that it can be crossed under certain conditions.

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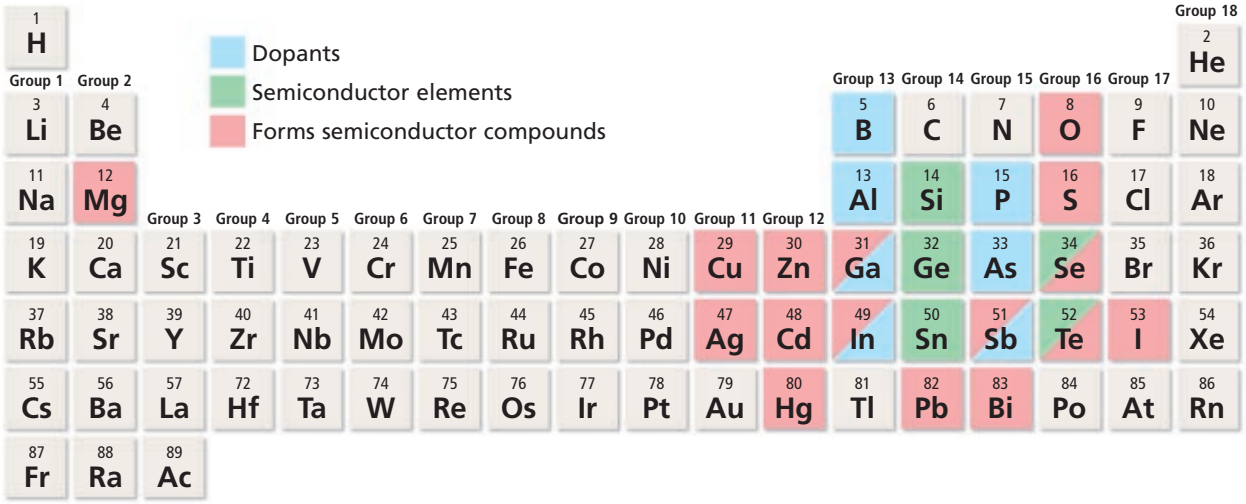
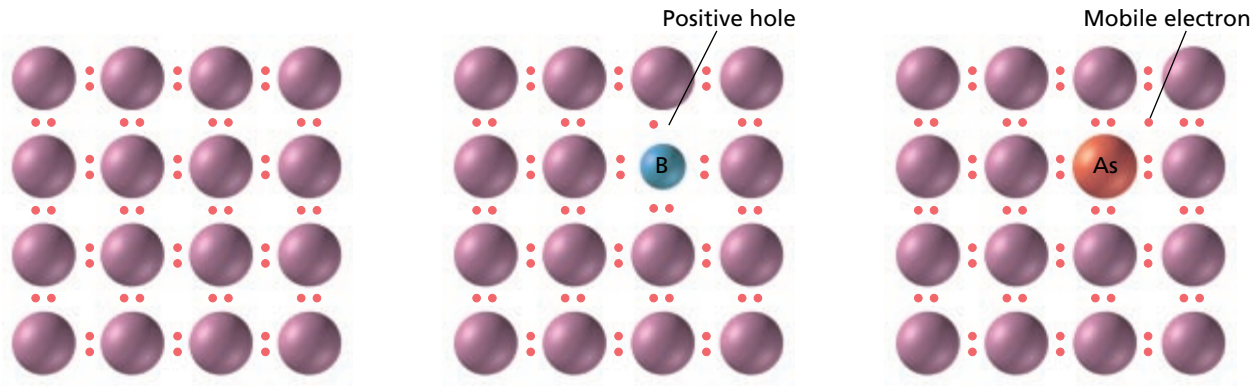


Semiconductor elements and dopants fall in the metalloid region of the periodic table. Semiconductor compounds often contain metals.

and a boron atom is a hole that a free electron can occupy. Because this hole "attracts" an electron, it is viewed as if it were positively charged. Semiconductors that are doped with boron, aluminum, or gallium are *p-type semiconductors,* the *p* standing for "positive." P-type semiconductors conduct electricity better than pure silicon because they provide spaces that moving electrons can occupy as they flow through the material.

Doping silicon with phosphorus or arsenic produces the opposite effect. When phosphorus is added to silicon, it forms four bonds to silicon atoms and has a nonbonding electron left over. This extra electron is free to move through the material when a voltage is applied, thus increasing its conductivity compared with pure silicon. These extra electrons have a negative charge. Therefore, the material is an *n-type semiconductor*. Compare these two types of semiconductors in the models below.



Each silicon atom in the pure crystal is surrounded by four pairs of electrons. The p-type semiconductor model contains an atom of boron with a hole that an electron can occupy. The n-type semiconductor model contains an atom of arsenic, which provides the extra electron that can move through the crystal.

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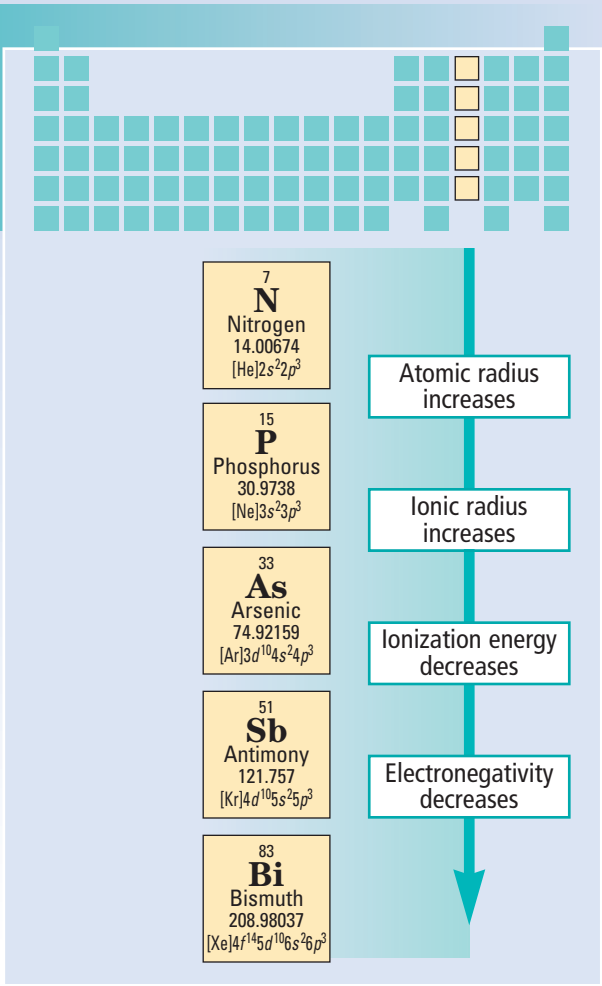
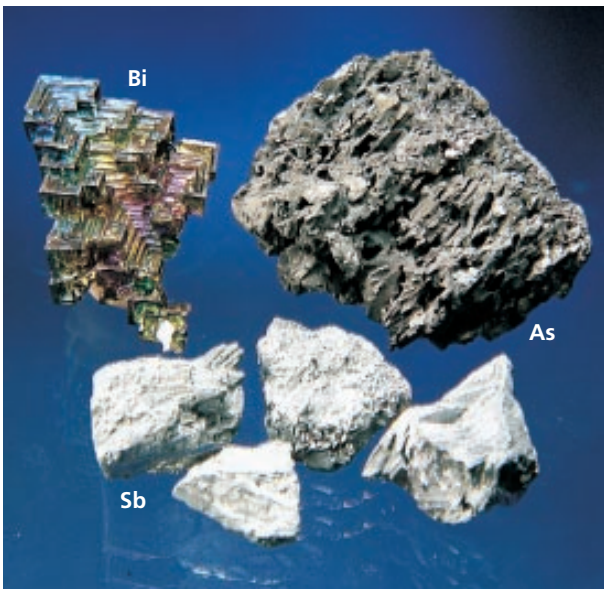
GROUP 15
NITROGEN FAMILY



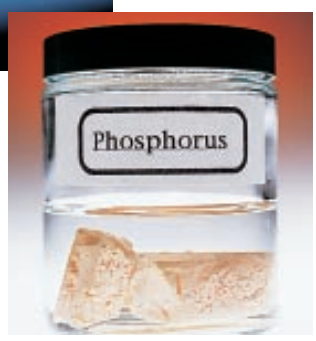
CHARACTERISTICS

- consist of two nonmetals (nitrogen and phosphorus), two metalloids (arsenic and antimony), and one metal (bismuth)
- Nitrogen is most commonly found as atmospheric N_2; phosphorus as phosphate rock; and arsenic, antimony, and bismuth as sulfides or oxides. Antimony and bismuth are also found as elements.
- range from very abundant elements (nitrogen and phosphorus) to relatively rare elements (arsenic, antimony, and bismuth)
- consist of atoms that contain five electrons in their outermost energy level
- tend to form covalent compounds, most commonly with oxidation numbers of +3 or +5
- exist in two or more allotropic forms, except nitrogen and bismuth
- are solids at room temperature, except nitrogen



You can see the contrast in physical properties among the elements of this family. Arsenic, antimony, and bismuth are shown.

Some matches contain phosphorus compounds in the match head. Safety matches contain phosphorus in the striking strip on the matchbox.



Phosphorus exists in three allotropic forms. White phosphorus must be kept underwater because it catches on fire when exposed to air. The red and black forms are stable in air.

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COMMON REACTIONS

With Oxygen to Form Oxides

Example: $P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s)$

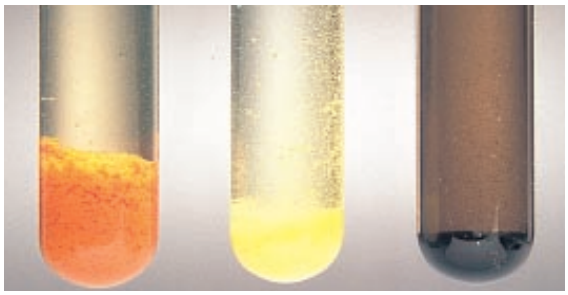
As, Sb, and Bi follow this reaction pattern, but as monatomic elements. N reacts as N_2 to form N_2O_3 and N_2O_5.

With Metals to Form Binary Compounds

Example: $3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$

ANALYTICAL TEST

Other than atomic absorption spectroscopy, there are no simple analytical tests for the presence of nitrogen or phosphorus compounds in a sample. Antimony produces a pale green color in a flame test, and arsenic produces a light blue color. Arsenic, antimony, and bismuth are recognized in qualitative analyses by their characteristic sulfide colors.



Formation of sulfides is the confirmatory qualitative analysis test for the presence of bismuth, antimony, and arsenic.

Arsenic flame test

Antimony flame test

PROPERTIES OF THE GROUP 15 ELEMENTS

	N	P*	As	Sb	Bi
Melting point (°C)	–209.86	44.1	817 (28 atm)	630.5	271.3
Boiling point (°C)	–195.8	280	613 (sublimes)	1750	1560 ± 5
Density (g/cm^3)	1.25×10^{-3}	1.82	5.727	6.684	9.80
Ionization energy (kJ/mol)	1402	1012	947	834	703
Atomic radius (pm)	75	110	122	143	151
Ionic radius (pm)	146 (N^{3-})	212 (P^{3-})	—	76 (Sb^{3+})	103 (Bi^{3+})
Common oxidation number in compounds	–3, +3, +5	–3, +3, +5	+3, +5	+3, +5	+3
Crystal structure†	cubic (as a solid)	cubic	rhombohedral	hcp	rhombohedral
Hardness (Mohs' scale)	none (gas)	—	3.5	3.0	2.25

* Data given apply to white phosphorus.
† Crystal structures are for the most common allotropes.

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APPLICATION *Biology*

Plants and Nitrogen

All organisms, including plants, require certain elements to survive and grow. These elements include carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, and several other elements needed in small amounts. An organism needs nitrogen to synthesize structural proteins, enzymes, and the nucleic acids DNA and RNA.

Carbon, hydrogen, and oxygen are available to plants from carbon dioxide in the air and from water in both the air and the soil. Nitrogen is necessary for plants' survival. Although nitrogen gas, N_2, makes up 78% of air, plants cannot take nitrogen out of the air and incorporate it into their cells, because the strong triple covalent bond in N_2 is not easily broken. Plants need nitrogen in the form of a compound that they can take in and use. The process of using atmospheric N_2 to make NH_3 is called *nitrogen fixation*. Several kinds of nitrogen-fixing bacteria live in the soil and in the root nodules of plants called legumes. Legumes obtain the nitrogen they need through a symbiotic relationship with nitrogen-fixing bacteria. Legumes include peas, beans, clover, alfalfa, and locust trees. The bacteria convert nitrogen into ammonia, NH_3, which is then absorbed by the host plants.

Because wheat, rice, corn, and potatoes cannot perform the same feat as legumes, these plants depend on nitrogen-fixing bacteria in the soil. Soil bacteria convert NH_3 into nitrate ions, NO_3^-, the form of nitrogen that can be absorbed and used by plants. These plants also often need nitrogen fertilizers to supplement the work of the bacteria. Besides supplying nitrogen, fertilizers are manufactured to contain phosphorus, potassium, and trace minerals.

Nitrogen-fixing bacteria,* Rhizobium, *live in these small nodules that grow on the roots of soybeans.

Soybeans are legumes that live in a symbiotic relationship with nitrogen-fixing bacteria.

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APPLICATION *Chemical Industry*

Fertilizers

Fertilizers can supply nitrogen to plants in the form of ammonium sulfate, ammonium nitrate, and urea, all of which are made from NH_3. Now you know why there is such a demand for ammonia. Though some soils contain sufficient concentrations of phosphorus and potassium, most soils need additional nitrogen for adequate plant growth. Ammonia, ammonium nitrate, or urea can fill that need.

Most fertilizers contain all three major plant nutrients N, P, and K, and are called *complete fertilizers*. A typical complete fertilizer might contain ammonium nitrate or sodium nitrate to provide nitrogen. Calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, or the anhydrous form of phosphoric acid, P_2O_5, can provide phosphorus. Potassium chloride, KCl, contains sufficient K_2O impurities to provide potassium.

The proportion of each major nutrient in a fertilizer is indicated by a set of three numbers printed on the container. These numbers are the N-P-K formula of the fertilizer and indicate the percentage of N, P, and K, respectively. A fertilizer graded as 6-12-6, for example, contains 6% nitrogen, 12% phosphorus, and 6% potassium by weight and all in the form of compounds.

Nitrogen stimulates overall plant growth. Phosphorus promotes root growth and flowering. Potassium regulates the structures in leaves that allow CO_2 to enter the leaf and O_2 and H_2O to exit. Fertilizers are available in N-P-K formulas best suited for their intended use. For example, plants that produce large amounts of carbohydrates (sugars) need more potassium than most other types of plants. Grain crops need higher concentrations of phosphorus. Lawn fertilizers applied in the spring are generally high in nitrogen to stimulate shoot growth in grasses. Lawn fertilizers applied in the fall of the year should have a higher phosphorus content to stimulate root growth during the winter.

TABLE 6A Some Commercial Fertilizers and Uses

Fertilizer composition (N-P-K)	Uses
1-2-1 ratio 10-20-10 15-30-15	early-spring application for trees and shrubs with flowers and fruit; general-purpose feedings of the following: cucumbers, peppers, tomatoes
3-1-2 ratio 12-4-8 15-5-10 21-7-4 16-4-8 20-5-10	lawns and general-purpose feedings of the following: trees, shrubs, most berries, apple trees, grapes, vines, walnut trees, broccoli, cabbage, carrots, onions
High nitrogen 33-0-0 21-0-0 40-4-4 36-6-6	pecan trees, lawns, early feedings of corn
Balanced 13-13-13	general purpose feeding of the following: broccoli, cabbage, melons, potatoes
Special purpose: acid-loving flowering shrubs 12-10-4	azaleas, rhododendrons, camellias, gardenias
Special purpose 18-24-16	roses
Special purpose: flowering 12-55-6	flowering plants and shrubs (annuals and perennials)
Special purpose: root growth 5-20-10	starter fertilizer for transplants

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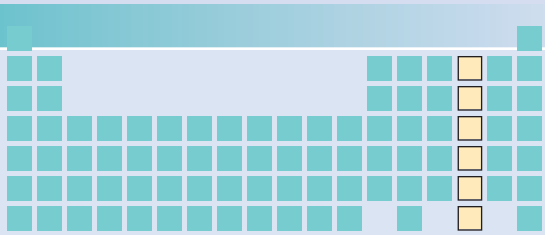
GROUP 16
OXYGEN FAMILY



CHARACTERISTICS

- occur naturally as elements and in combined states
- consist of three nonmetals (oxygen, sulfur, and selenium), one metalloid (tellurium), and one metal (polonium)
- consist of atoms that have six electrons in their outermost energy level
- tend to form covalent compounds with other elements
- exist in several allotropic forms
- tend to exist as diatomic and polyatomic molecules, such as O_2, O_3, S_6, S_8, and Se_8
- commonly exist in compounds with the –2 oxidation state but often exhibit other oxidation states

8
O
Oxygen
15.9994
$[He]2s^22p^4$

16
S
Sulfur
32.066
$[Ne]3s^23p^4$

34
Se
Selenium
78.96
$[Ar]3d^{10}4s^24p^4$

52
Te
Tellurium
127.60
$[Kr]4d^{10}5s^25p^4$

84
Po
Polonium
(208.9824)
$[Xe]4f^{14}5d^{10}6s^26p^4$

Atomic radius increases

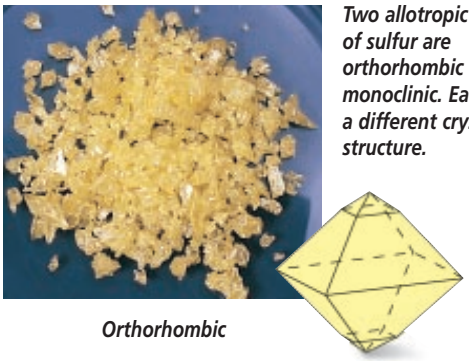
Ionic radius increases

Ionization energy decreases

Electronegativity decreases

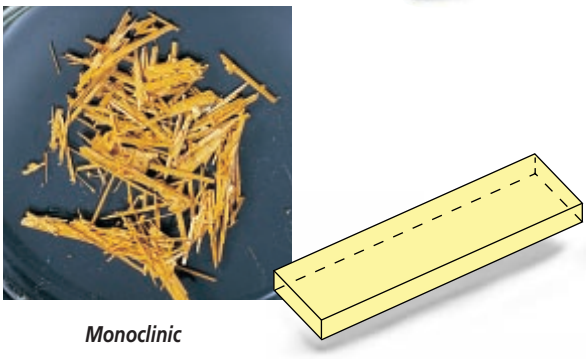
Sulfur is found naturally in underground deposits and in the steam vents near volcanoes.

Sulfur exists in combined forms in many minerals. Iron pyrite, FeS_2, black galena, PbS, and yellow orpiment, As_2S_3, are shown.



Two allotropic forms of sulfur are orthorhombic and monoclinic. Each has a different crystal structure.

Orthorhombic



Monoclinic

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COMMON REACTIONS

With Metals to Form Binary Compounds

Example: $8Mg(s) + S_8(l) \longrightarrow 8MgS(s)$

O_2, Se, and Te follow this pattern in reacting with Na, K, Ca, Mg, and Al.

With Oxygen to Form Oxides

Example: $Se(s) + O_2(g) \longrightarrow SeO_2(s)$

S, Te, and Po follow this pattern. S, Se, and Te can form SO_3, SeO_3, and TeO_3.

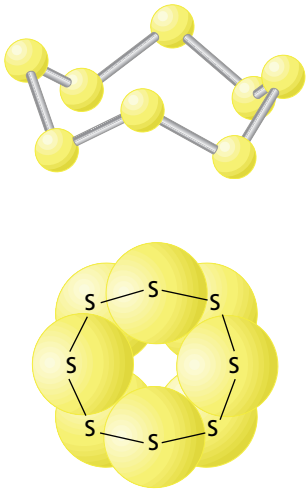
With Halogens to Form Binary Compounds

Example: $S_8(l) + 8Cl_2(g) \longrightarrow 8SCl_2(l)$

O, Se, Te, and Po follow this pattern in reacting with F_2, Cl_2, Br_2, and I_2.

With Hydrogen to Form Binary Compounds

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$



Sulfur exists as S_8 molecules in which the atoms are bonded in a ring, as shown by the ball-and-stick and space-filling models.

ANALYTICAL TEST

Other than atomic absorption spectroscopy, there is no simple analytical test to identify all elements of this family. Selenium and tellurium can be identified by flame tests. A light blue flame is characteristic of selenium, and a green flame is characteristic of tellurium. Oxygen can be identified by the splint test, in which a glowing splint bursts into flame when thrust into oxygen. Elemental sulfur is typically identified by its physical characteristics, especially its color and its properties when heated. It melts to form a viscous brown liquid and burns with a blue flame.

A glowing splint thrust into oxygen bursts into a bright flame.

Sulfur burns with a characteristically deep blue flame.

Molten sulfur returns to its orthorhombic form upon cooling.

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PROPERTIES OF THE GROUP 16 ELEMENTS

	O	S	Se	Te	Po
Melting point (°C)	–218.4	119.0	217	449.8	254
Boiling point (°C)	–182.962	444.674	685	989.9	962
Density (g/cm^3)	1.429×10^{-3}	1.96	4.82	6.24	9.4
Ionization energy (kJ/mol)	1314	1000	941	869	812
Atomic radius (pm)	73	103	119	142	168
Ionic radius (pm)	140	184	198	221	—
Common oxidation number in compounds	–2	–2, +4, +6	–2, +2, +4, +6	–2, +2, +4, +6	–2, +2, +4, +6
Crystal structure*	orthorhombic, rhombohedral, cubic (when solid)	orthorhombic, monoclinic	hexagonal	hexagonal	cubic, rhombohedral
Hardness (Mohs' scale)	none (gas)	2.0	2.0	2.3	—

* Most elements of this family can have more than one crystal structure.

APPLICATION *Chemical Industry*

Oxides

Oxides of the reactive metals are ionic compounds. The oxide ion from any soluble oxide reacts immediately with water to form hydroxide ions as represented by the following equation.

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$$

The reactive metal oxides of Groups 1 and 2 react vigorously with water and release a large amount of heat. The product of the reaction is a metal hydroxide. The following equation is an example of this reaction.

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

A basic oxide can be thought of as the dehydrated form of a hydroxide base. Oxides of the less reactive metals, such as magnesium, can be prepared by using thermal decomposition to drive off the water.

$$Mg(OH)_2(s) \xrightarrow{heat} MgO(s) + H_2O(g)$$

Hydroxides of the reactive metals of Group 1 are too stable to decompose in this manner.

If a hydroxide formed by a metal oxide is water-soluble, it dissolves to form a basic solution. An oxide that reacts with water to form a basic solution is called a basic oxide or a basic anhydride. Table 7A on the next page lists oxides that form basic solutions with water.

Molecular Oxides

Nonmetals, located on the right side of the periodic table, form molecular oxides. For example, sulfur forms two gaseous oxides: sulfur dioxide, SO_2, and sulfur trioxide, SO_3. In reactions typical of nonmetal oxides, each of the sulfur oxides reacts with water to form an oxyacid.

An oxide that reacts with water to form an acid is called an acidic oxide or an acid anhydride. As with the basic anhydrides, each acid anhydride can be thought of as the dehydrated form of the appropriate oxyacid. For example, when sulfuric acid decomposes, the loss of H_2O leaves the oxide SO_3, which is an anhydride.

$$H_2SO_4(aq) \xrightarrow{heat} H_2O(g) + SO_3(g)$$

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Amphoteric Oxides

Table 7A lists some common oxides of main-group elements. You can see that the active metal oxides are basic and that the nonmetal oxides are acidic. Between these lies a group of oxides, the *amphoteric oxides*. The bonding in amphoteric oxides is intermediate between ionic and covalent bonding. As a result, oxides of this type show behavior intermediate between that of acidic oxides and basic oxides, and react as both acids and bases.

Aluminum oxide, Al_2O_3, is a typical amphoteric oxide. With hydrochloric acid, aluminum oxide acts as a base. The reaction produces a salt and water.

$$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$$

With aqueous sodium hydroxide, aluminum oxide acts as an acid. The reaction forms a soluble ionic compound and water. That compound contains aluminate ions, AlO_2^-. (The AlO_2^- formula is used here rather than the more precise hydrated aluminate formula, $Al(OH)_4^-$.)

$$Al_2O_3(s) + 2NaOH(aq) \longrightarrow 2NaAlO_2(aq) + H_2O(l)$$

Reactions of Oxides

In the reaction between an acid and a metal oxide, the products are a salt and water—the same as the products in a neutralization reaction. For example, when magnesium oxide reacts with dilute sulfuric acid, magnesium sulfate and water are produced.

$$MgO(s) + H_2SO_4(dil.\ aq) \longrightarrow MgSO_4(aq) + H_2O(l)$$

The reaction between a basic metal oxide, such as MgO, and an acidic nonmetal oxide, such as CO_2, tends to produce an oxygen-containing salt. The dry oxides are mixed and heated without water. Salts such as metal carbonates, phosphates, and sulfates can be made by this synthesis reaction.

$$MgO(s) + CO_2(g) \longrightarrow MgCO_3(s)$$

$$6CaO(s) + P_4O_{10}(s) \longrightarrow 2Ca_3(PO_4)_2(s)$$

$$CaO(s) + SO_3(g) \longrightarrow CaSO_4(s)$$

Reactions of Hydroxides with Nonmetal Oxides

Nonmetal oxides tend to be acid anhydrides. The reaction of a hydroxide base with a nonmetal oxide is an acid-base reaction. The product is either a salt or a salt and water, depending on the identities and relative quantities of reactants. For example, 2 mol of the hydroxide base sodium hydroxide and 1 mol of the nonmetal oxide carbon dioxide form sodium carbonate, which is a salt, and water.

$$CO_2(g) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

However, if sodium hydroxide is limited, only sodium hydrogen carbonate is produced.

$$CO_2(g) + NaOH(aq) \longrightarrow NaHCO_3(aq)$$

TABLE 7A Periodicity of Acidic and Basic Oxides of Main-Group Elements

	Group Number					
1	**2**	**13**	**14**	**15**	**16**	**17**
Li_2O basic	BeO amphoteric	B_2O_3 acidic	CO_2 acidic	N_2O_5 acidic		
Na_2O basic	MgO basic	Al_2O_3 amphoteric	SiO_2 acidic	P_4O_{10} acidic	SO_3 acidic	Cl_2O acidic
K_2O basic	CaO basic	Ga_2O_3 amphoteric	GeO_2 amphoteric	As_4O_6 amphoteric	SeO_3 acidic	
Rb_2O basic	SrO basic	In_2O_3 basic	SnO_2 amphoteric	Sb_4O_6 amphoteric	TeO_3 acidic	I_2O_5 acidic
Cs_2O basic	BaO basic	Tl_2O_3 basic	PbO_2 amphoteric	Bi_2O_3 basic		

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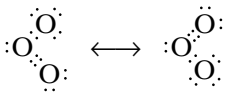
APPLICATION *The Environment*

Ozone

Ozone, O_3, is an allotrope of oxygen that is important for life on Earth. Like O_2, O_3 is a gas at room temperature. However, unlike O_2, O_3 is a poisonous bluish gas with an irritating odor at high concentrations. The triatomic ozone molecule is angular (bent) with a bond angle of about 116.5°. The O—O bonds in ozone are shorter and stronger than a single bond, but longer and weaker than a double bond. The ozone molecule is best represented by two resonance hybrid structures.



Ozone forms naturally in Earth's atmosphere more than 24 km above the Earth's surface in a layer called the stratosphere. There, O_2 molecules absorb energy from ultraviolet light and split into free oxygen atoms.

$$O_2(g) \xrightarrow{\text{ultraviolet light}} 2O$$

A free oxygen atom has an unpaired electron and is highly reactive. A chemical species that has one or more unpaired or unshared electrons is referred to as a *free radical*. A free radical is a short-lived fragment of a molecule. The oxygen free radical can react with a molecule of O_2 to produce an ozone molecule.

$$O + O_2(g) \longrightarrow O_3(g)$$

A molecule of O_3 can then absorb ultraviolet light and split to produce O_2 and a free oxygen atom.

$$O_3(g) \xrightarrow{\text{ultraviolet light}} O_2(g) + O$$

The production and breakdown of ozone in the stratosphere are examples of *photochemical* processes, in which light causes a chemical reaction.

In this way, O_3 is constantly formed and destroyed in the stratosphere, and its concentration is determined by the balance among these reactions. The breakdown of ozone absorbs the sun's intense ultraviolet light in the range of wavelengths between 290 nm and 320 nm. Light of these wavelengths damages and kills living cells, so if these wavelengths were to reach Earth's surface in large amounts, life would be impossible. Even now, the normal amount of ultraviolet light reaching Earth's surface is a major cause of skin cancer and the damage to DNA molecules that causes mutations. One life-form that is very sensitive to ultraviolet radiation is the phytoplankton in the oceans. These organisms carry out photosynthesis and are the first level of oceanic food webs.

Ozone and Air Pollution

Ozone in the lower atmosphere is a harmful pollutant. Ozone is highly reactive and can oxidize organic compounds. The products of these reactions are harmful substances that, when mixed with air, water vapor, and dust, make up *photochemical smog*. This mixture is the smog typically found in cities.

Typically, ozone is produced in a complex series of reactions involving unburned hydrocarbons and nitrogen oxides given off from engines in the form of exhaust and from fuel-burning power plants. When fuel burns explosively in the cylinder of an internal-combustion engine, some of the nitrogen in the cylinder also combines with oxygen to form NO, a very reactive nitrogen-oxide free radical.

$$N_2(g) + O_2(g) \longrightarrow 2NO$$

When the free radical reaches the air, it reacts with oxygen to produce NO_2 radicals, which react with water in the air to produce HNO_3.

$$2NO + O_2(g) \longrightarrow 2NO_2$$
$$3NO_2 + H_2O(l) \longrightarrow NO + 2HNO_3(aq)$$

In sunlight, nitrogen dioxide decomposes to give nitric oxide and an atom of oxygen. Note that the NO produced is free to undergo the previous reaction once more.

$$NO_2 \xrightarrow{\text{sunlight}} NO + O$$

Just as it is in the stratosphere, a free oxygen atom in the lower atmosphere is highly reactive and reacts with a molecule of diatomic oxygen to form ozone.

$$O + O_2(g) \longrightarrow O_3(g)$$

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APPLICATION *Chemical Industry*

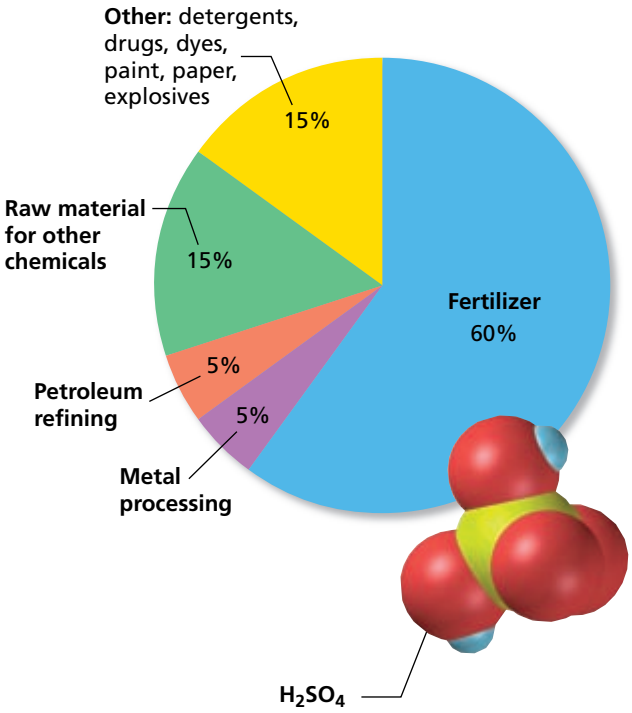
Sulfuric Acid

Sulfuric acid is the so-called "king of chemicals" because it is produced in the largest volume in the United States. It is produced by the contact process. This process starts with the production of SO_2 by burning sulfur or roasting iron pyrite, FeS_2. The purified sulfur dioxide is mixed with air and passed through hot iron pipes containing a catalyst. The contact between the catalyst, SO_2, and O_2 produces sulfur trioxide, SO_3, and gives the contact process its name. SO_3 is dissolved in concentrated H_2SO_4 to produce pyrosulfuric acid, $H_2S_2O_7$.

$$SO_3(g) + H_2SO_4(aq) \longrightarrow H_2S_2O_7(aq)$$

The pyrosulfuric acid is then diluted with water to produce sulfuric acid.

$$H_2S_2O_7(aq) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$$



Important uses of the U.S. supply of sulfuric acid

Properties and Uses of Sulfuric Acid

Concentrated sulfuric acid is a good oxidizing agent. During the oxidation process, sulfur is reduced from +6 to +4 or –2. The change in oxidation state for a reaction depends on the concentration of the acid and on the nature of the reducing agent used in the reaction.

Sulfuric acid is also an important dehydrating agent. Gases that do not react with H_2SO_4 can be dried by being bubbled through concentrated sulfuric acid. Organic compounds, like sucrose, are dehydrated to leave carbon, as shown by the following reaction.

$$C_{12}H_{22}O_{11}(s) + 11H_2SO_4(aq) \longrightarrow 12C(s) + 11H_2SO_4{\cdot}H_2O(l)$$

The decomposition of sucrose proceeds rapidly, as shown in Figure 21-9 on page 684.

About 60% of the sulfuric acid produced in this country is used to make superphosphate, which is a mixture of phosphate compounds used in fertilizers.

TABLE 7B Top Ten Chemicals Produced in the U.S.

Rank	Chemical	Physical state	Formula
1	sulfuric acid	*l*	H_2SO_4
2	nitrogen	*g*	N_2
3	oxygen	*g*	O_2
4	ethylene	*g*	C_2H_4
5	calcium oxide (lime)	*s*	CaO
6	ammonia	*g*	NH_3
7	phosphoric acid	*l*	H_3PO_4
8	sodium hydroxide	*s*	NaOH
9	propylene	*g*	C_3H_6
10	chlorine	*g*	Cl_2

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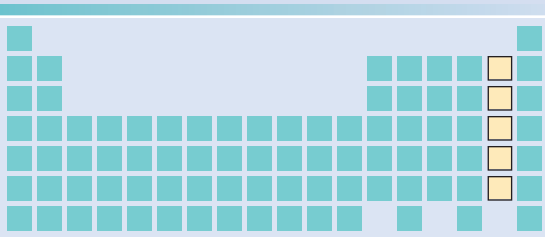
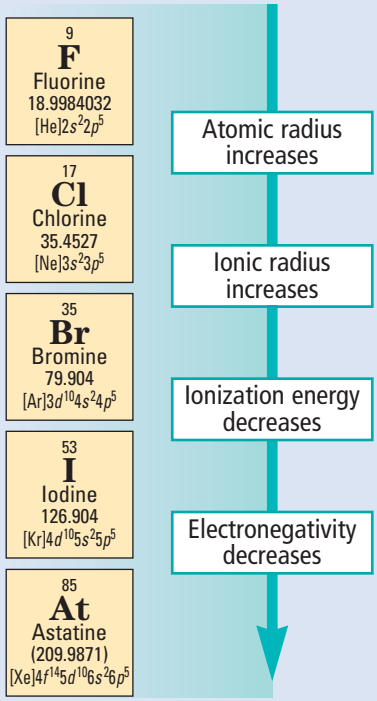
GROUP 17
HALOGEN FAMILY



CHARACTERISTICS

- are all nonmetals and occur in combined form in nature, mainly as metal halides
- are found in the rocks of Earth's crust and dissolved in sea water
- range from fluorine, the 13th most abundant element, to astatine, which is one of the rarest elements
- exist at room temperature as a gas (F_2 and Cl_2), a liquid (Br_2), and a solid (I_2 and At)
- consist of atoms that have seven electrons in their outermost energy level
- tend to gain one electron to form a halide, X^- ion, but also share electrons and have positive oxidation states
- are reactive, with fluorine being the most reactive of all nonmetals



Halogens are the only family that contains elements representing all three states of matter at room temperature. Chlorine is a yellowish green gas; bromine is a reddish brown liquid; and iodine is a purple-black solid.

Iodine sublimes to produce a violet vapor that recrystallizes on the bottom of the evaporating dish filled with ice.

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COMMON REACTIONS*

Chlorine combines readily with iron wool, which ignites in chlorine gas to form $FeCl_3$.

With Metals to Form Halides

Example: $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
Example: $Sn(s) + 2F_2(g) \longrightarrow SnF_4(s)$
The halide formula depends on the oxidation state of the metal.

With Hydrogen to Form Hydrogen Halides

Example: $H_2(g) + F_2(g) \rightarrow 2HF(g)$
Cl_2, Br_2, and I_2 also follow this pattern.

With Nonmetals and Metalloids to Form Halides

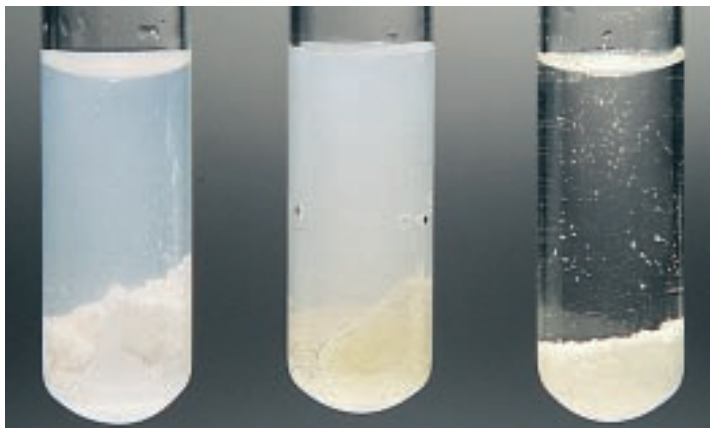
Example: $Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(s)$
Example: $N_2(g) + 3F_2(g) \longrightarrow 2NF_3(g)$
Example: $P_4(s) + 6Br_2(l) \longrightarrow 4PBr_3(s)$
The formula of the halide depends on the oxidation state of the metalloid or nonmetal.

With Other Halogens to Form Interhalogen Compounds

Example: $Br_2(l) + 3F_2(g) \longrightarrow 2BrF_3(l)$

* Chemists assume that astatine undergoes similar reactions, but few chemical tests have been made.

Hydrofluoric acid is used to etch patterns into glass.



Shown here from left to right are precipitates of AgCl, AgBr, and AgI.

ANALYTICAL TEST

As with most elements, the presence of each of the halogens can be determined by atomic absorption spectroscopy. Fluorides react with concentrated sulfuric acid, H_2SO_4, to release hydrogen fluoride gas. Three of the halide ions can be identified in solution by their reactions with silver nitrate.

$Cl^-(aq) + Ag^+(aq) \longrightarrow AgCl(s)$
$Br^-(aq) + Ag^+(aq) \longrightarrow AgBr(s)$
$I^-(aq) + Ag^+(aq) \longrightarrow AgI(s)$

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PROPERTIES OF THE GROUP 17 ELEMENTS

	F	Cl	Br	I	At
Melting point (°C)	–219.62	–100.98	–7.2	113.5	575.2
Boiling point (°C)	–188.14	–34.6	58.78	184.35	610
Density (g/cm^3)	1.69×10^{-3}	3.214×10^{-3}	3.119	4.93	not known
Ionization energy (kJ/mol)	1681	1251	1140	1008	—
Atomic radius (pm)	72	100	114	133	140
Ionic radius (pm)	133	181	196	220	—
Common oxidation number in compounds	–1	–1, +1, +3, +5, +7	–1, +1, +3, +5, +7	–1, +1, +3, +5, +7	–1, +5
Crystal structure	cubic	orthorhombic	orthorhombic	orthorhombic	not known

APPLICATION *The Environment*

Chlorine in Water Treatment

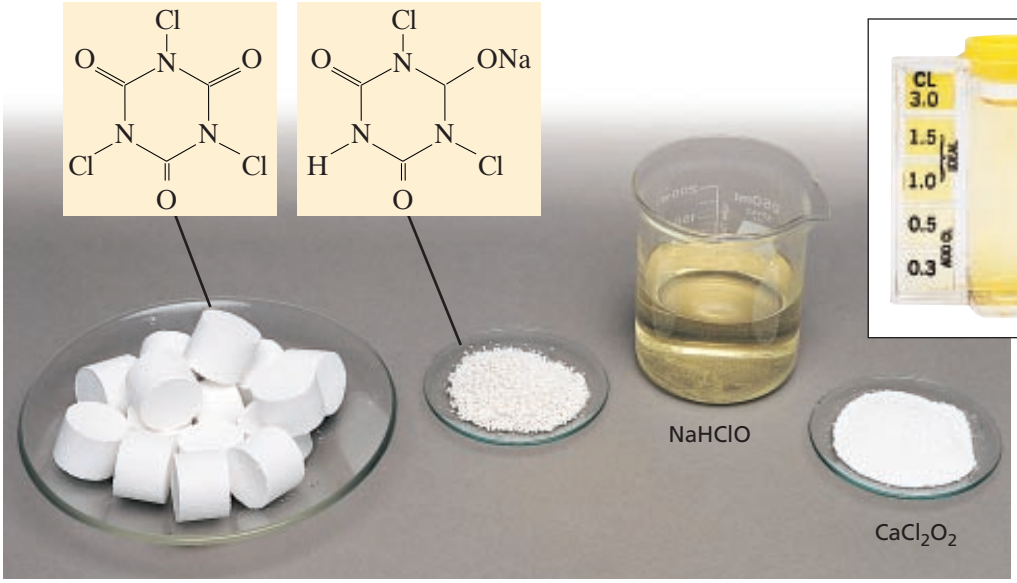
For more than a century, communities have treated their water to reduce the amount of toxic substances in the water and to prevent disease. A treatment process widely used in the United States is chlorination. All halogens kill bacteria and other microorganisms. Chlorine, however, is the only halogen acceptable for large-scale treatment of public water supplies.

When chlorine is added to water, the following reaction produces HCl and hypochlorous acid, HOCl.

$$Cl_2(g) + H_2O(l) \longrightarrow HCl(aq) + HOCl(aq)$$

Hypochlorous acid is a weak acid that ionizes to give hydrogen ions and hypochlorite ions, OCl^-.

$$HOCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + OCl^-(aq)$$



Swimming pools are routinely tested to be sure the chlorine level is safe.

The "chlorine" used in swimming pools is really the compounds shown above and not chlorine at all.

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The OCl^- ions are strong oxidizing agents that can destroy microorganisms.

In some water-treatment plants, calcium hypochlorite, $Ca(ClO)_2$, a salt of hypochlorous acid, is added to water to provide OCl^- ions. Similar treatments are used in swimming pools.

Nearly a hundred cities in the United States and thousands of communities in Europe use chlorine in the form of chlorine dioxide, ClO_2, as their primary means of disinfecting water. The main drawback to the use of ClO_2 is that it is unstable and cannot be stored. Instead, ClO_2 must be prepared on location by one of the following reactions involving sodium chlorite, $NaClO_2$.

$$10NaClO_2(aq) + 5H_2SO_4(aq) \longrightarrow 8ClO_2(g) + 5Na_2SO_4(aq) + 2HCl(aq) + 4H_2O(l)$$

$$2NaClO_2(aq) + Cl_2(g) \longrightarrow 2ClO_2(g) + 2NaCl(aq)$$

The expense of using ClO_2 makes it less desirable than Cl_2 in water-treatment systems unless there are other considerations. For example, the use of ClO_2 is likely to result in purified water with less of the aftertaste and odor associated with water purified by Cl_2.

Fluoride and Tooth Decay

In the 1940s, scientists noticed that people living in communities that have natural water supplies with high concentrations of fluoride ions, F^-, have significantly lower rates of dental caries (tooth decay) than most of the population.

In June 1944, a study on the effects of water fluoridation began in two Michigan cities, Muskegon and Grand Rapids, where the natural level of fluoride in drinking water was low (about 0.05 ppm). In Grand Rapids, sodium fluoride, NaF, was added to the drinking water to raise levels to 1.0 ppm. In Muskegon, no fluoride was added. Also included in the study was Aurora, Illinois, a city that was similar to Grand Rapids and Muskegon, except that it had a natural F^- concentration of 1.2 ppm in the water supply. After 10 years, the rate of tooth decay in Grand Rapids had dropped far below that in Muskegon and was about the same as it was in Aurora.

Tooth enamel is made of a strong, rocklike material consisting mostly of calcium hydroxyphosphate, $Ca_5(PO_4)_3(OH)$, also known as apatite. Apatite is an insoluble and very hard compound—ideal for tooth enamel. Sometimes, however, saliva becomes more acidic, particularly after a person eats a high-sugar meal. Acids ionize to produce hydronium ions, which react with the hydroxide ion, OH^-, in the apatite to form water. The loss of OH^- causes the apatite to dissolve.

$$Ca_5(PO_4)_3(OH)(s) + H_3O^+(aq) \longrightarrow 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + 2H_2O(l)$$

Saliva supplies more OH^- ions, and new apatite is formed, but slowly.

If fluoride ions are present in saliva, some fluorapatite, $Ca_5(PO_4)_3F$, also forms.

$$5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + F^-(aq) \longrightarrow Ca_5(PO_4)_3F(s)$$

Fluorapatite resists attack by acids, so the tooth enamel resists decay better than enamel containing no fluoride.

When the beneficial effect of fluoride had been established, public health authorities proposed that fluoride compounds be added to water supplies in low-fluoride communities. Fluoridation started in the 1950s, and by 1965, nearly every medical and dental association in the United States had endorsed fluoridation of water supplies. In the past decade, however, that trend slowed as opposition to fluoridation grew.

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APPENDIX A

TABLE A-1 SI MEASUREMENT

Metric Prefixes

Prefix	Symbol	Factor of Base Unit
giga	G	1 000 000 000
mega	M	1 000 000
kilo	k	1 000
hecto	h	100
deka	da	10
deci	d	0.1
centi	c	0.01
milli	m	0.001
micro	μ	0.000 001
nano	n	0.000 000 001
pico	p	0.000 000 000 001

Mass

1 kilogram (kg)	= SI base unit of mass
1 gram (g)	= 0.001 kg
1 milligram (mg)	= 0.000 001 kg
1 microgram (μg)	= 0.000 000 001 kg

Length

1 kilometer (km)	= 1 000 m
1 meter (m)	= SI base unit of length
1 centimeter (cm)	= 0.01 m
1 millimeter (mm)	= 0.001 m
1 micrometer (μm)	= 0.000 001 m
1 nanometer (nm)	= 0.000 000 001 m
1 picometer (pm)	= 0.000 000 000 001 m

Area

1 square kilometer (km^2)	= 100 hectares (ha)
1 hectare (ha)	= 10 000 square meters (m^2)
1 square meter (m^2)	= 10 000 square centimeters (cm^2)
1 square centimeter (cm^2)	= 100 square millimeters (mm^2)

Volume

1 liter (L)	= common unit for liquid volume (not SI)
1 cubic meter (m^3)	= 1000 L
1 kiloliter (kL)	= 1000 L
1 milliliter (mL)	= 0.001 L
1 milliliter (mL)	= 1 cubic centimeter (cm^3)

TABLE A-2 ABBREVIATIONS

amu	=	atomic mass unit (mass)
atm	=	atmosphere (pressure, non-SI)
Bq	=	becquerel (nuclear activity)
°C	=	degree Celsius (temperature)
J	=	joule (energy)
K	=	kelvin (temperature, thermodynamic)
mol	=	mole (quantity)
M	=	molarity (concentration)
N	=	newton (force)
Pa	=	pascal (pressure)
s	=	second (time)
V	=	volt (electric potential difference)

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TABLE A-3 SYMBOLS

Symbol		Meaning
α	=	helium nucleus (also ^4_2He) emission from radioactive materials
β	=	electron (also $^0_{-1}e$) emission from radioactive materials
γ	=	high-energy photon emission from radioactive materials
Δ	=	change in a given quantity (e.g., ΔH for change in enthalpy)
c	=	speed of light in vacuum
c_p	=	specific heat capacity (at constant pressure)
D	=	density
E_a	=	activation energy
E^0	=	standard electrode potential
E^0 cell	=	standard potential of an electrochemical cell
G	=	Gibbs free energy
ΔG^0	=	standard free energy of reaction
ΔG^0_f	=	standard molar free energy of formation
H	=	enthalpy
ΔH^0	=	standard enthalpy of reaction
ΔH^0_f	=	standard molar enthalpy of formation
K_a	=	ionization constant (acid)
K_b	=	dissociation constant (base)
K_{eq}	=	equilibrium constant
K_{sp}	=	solubility-product constant
KE	=	kinetic energy
m	=	mass
N_A	=	Avogadro's number
n	=	number of moles
P	=	pressure
pH	=	measure of acidity ($-\log[H_3O^+]$)
R	=	ideal gas law constant
S	=	entropy
S^0	=	standard molar entropy
T	=	temperature (thermodynamic, in kelvins)
t	=	temperature (± degrees Celsius)
V	=	volume
v	=	velocity

TABLE A-4 PHYSICAL CONSTANTS

Quantity	Symbol	Value
Atomic mass unit	amu	$1.660\ 5402 \times 10^{-27}$ kg
Avogadro's number	N_A	$6.022\ 137 \times 10^{23}$/mol
Electron rest mass	m_e	$9.109\ 3897 \times 10^{-31}$ kg 5.4858×10^{-4} amu
Ideal gas law constant	R	8.314 L • kPa/mol • K 0.0821 L • atm/mol • K
Molar volume of ideal gas at STP	V_M	22.414 10 L/mol
Neutron rest mass	m_n	$1.674\ 9286 \times 10^{-27}$ kg 1.008 665 amu
Normal boiling point of water	T_b	373.15 K = 100.0°C
Normal freezing point of water	T_f	273.15 K = 0.00°C
Planck's constant	h	$6.626\ 076 \times 10^{-34}$ J • s
Proton rest mass	m_p	$1.672\ 6231 \times 10^{-27}$ kg 1.007 276 amu
Speed of light in a vacuum	c	$2.997\ 924\ 58 \times 10^8$ m/s
Temperature of triple point of water		273.16 K = 0.01°C

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TABLE A-5 HEAT OF COMBUSTION

Substance	Formula	State	ΔH_c
hydrogen	H_2	*g*	–285.8
graphite	C	*s*	–393.5
carbon monoxide	CO	*g*	–283.0
methane	CH_4	*g*	–890.8
ethane	C_2H_6	*g*	–1560.7
propane	C_3H_8	*g*	–2219.2
butane	C_4H_{10}	*g*	–2877.6
pentane	C_5H_{12}	*g*	–3535.6
hexane	C_6H_{14}	*l*	–4163.2
heptane	C_7H_{16}	*l*	–4817.0
octane	C_8H_{18}	*l*	–5470.5
ethene (ethylene)	C_2H_4	*g*	–1411.2
propene (propylene)	C_3H_6	*g*	–2058.0
ethyne (acetylene)	C_2H_2	*g*	–1301.1
benzene	C_6H_6	*l*	–3267.6
toluene	C_7H_8	*l*	–3910.3
naphthalene	$C_{10}H_8$	*s*	–5156.3
anthracene	$C_{14}H_{10}$	*s*	–7076.5
methanol	CH_3OH	*l*	–726.1
ethanol	C_2H_5OH	*l*	–1366.8
ether	$(C_2H_5)_2O$	*l*	–2751.1
formaldehyde	CH_2O	*g*	–570.7
glucose	$C_6H_{12}O_6$	*s*	–2803.0
sucrose	$C_{12}H_{22}O_{11}$	*s*	–5640.9

ΔH_c = heat of combustion of the given substance. All values of ΔH_c are expressed as kJ/mol of substance oxidized to $H_2O(l)$ and/or $CO_2(g)$ at constant pressure and 25°C.
s = solid, *l* = liquid, *g* = gas

TABLE A-6 THE ELEMENTS—SYMBOLS, ATOMIC NUMBERS, AND ATOMIC MASSES

Name of element	Symbol	Atomic number	Atomic mass
actinium	Ac	89	[227.0278]
aluminum	Al	13	26.981539
americium	Am	95	[243.0614]
antimony	Sb	51	121.757
argon	Ar	18	39.948
arsenic	As	33	74.92159
astatine	At	85	[209.9871]
barium	Ba	56	137.327
berkelium	Bk	97	[247.0703]
beryllium	Be	4	9.012182
bismuth	Bi	83	208.98037
bohrium	Bh	107	[262.12]
boron	B	5	10.811
bromine	Br	35	79.904
cadmium	Cd	48	112.411
calcium	Ca	20	40.078
californium	Cf	98	[251.0796]
carbon	C	6	12.011
cerium	Ce	58	140.115
cesium	Cs	55	132.90543
chlorine	Cl	17	35.4527
chromium	Cr	24	51.9961
cobalt	Co	27	58.93320
copper	Cu	29	63.546
curium	Cm	96	[247.0703]
dubnium	Db	105	[262.114]
dysprosium	Dy	66	162.50
einsteinium	Es	99	[252.083]
erbium	Er	68	167.26
europium	Eu	63	151.966
fermium	Fm	100	[257.0951]
fluorine	F	9	18.9984032
francium	Fr	87	[223.0197]
gadolinium	Gd	64	157.25
gallium	Ga	31	69.723
germanium	Ge	32	72.61
gold	Au	79	196.96654
hafnium	Hf	72	178.49
hassium	Hs	108	[265]
helium	He	2	4.002602
holmium	Ho	67	164.930
hydrogen	H	1	1.00794
indium	In	49	114.818
iodine	I	53	126.904
iridium	Ir	77	192.22
iron	Fe	26	55.847

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TABLE A-6 CONTINUED

Name of element	Symbol	Atomic number	Atomic mass
krypton	Kr	36	83.80
lanthanum	La	57	138.9055
lawrencium	Lr	103	[262.11]
lead	Pb	82	207.2
lithium	Li	3	6.941
lutetium	Lu	71	174.967
magnesium	Mg	12	24.3050
manganese	Mn	25	54.93805
meitnerium	Mt	109	[266]
mendelevium	Md	101	[258.10]
mercury	Hg	80	200.59
molybdenum	Mo	42	95.94
neodymium	Nd	60	144.24
neon	Ne	10	20.1797
neptunium	Np	93	[237.0482]
nickel	Ni	28	58.6934
niobium	Nb	41	92.90638
nitrogen	N	7	14.00674
nobelium	No	102	[259.1009]
osmium	Os	76	190.23
oxygen	O	8	15.9994
palladium	Pd	46	106.42
phosphorus	P	15	30.9738
platinum	Pt	78	195.08
plutonium	Pu	94	[244.0642]
polonium	Po	84	[208.9824]
potassium	K	19	39.0983
praseodymium	Pr	59	140.908
promethium	Pm	61	[144.9127]
protactinium	Pa	91	231.03588
radium	Ra	88	[226.0254]
radon	Rn	86	[222.0176]
rhenium	Re	75	186.207
rhodium	Rh	45	102.906
rubidium	Rb	37	85.4678
ruthenium	Ru	44	101.07
rutherfordium	Rf	104	[261.11]
samarium	Sm	62	150.36
scandium	Sc	21	44.955910
seaborgium	Sg	106	[263.118]
selenium	Se	34	78.96
silicon	Si	14	28.0855
silver	Ag	47	107.8682
sodium	Na	11	22.989768
strontium	Sr	38	87.62
sulfur	S	16	32.066
tantalum	Ta	73	180.9479
technetium	Tc	43	[97.9072]
tellurium	Te	52	127.60
terbium	Tb	65	158.92534
thallium	Tl	81	204.3833
thorium	Th	90	232.0381
thulium	Tm	69	168.93421
tin	Sn	50	118.710
titanium	Ti	22	47.88
tungsten	W	74	183.84
uranium	U	92	238.0289
vanadium	V	23	50.9415
xenon	Xe	54	131.29
ytterbium	Yb	70	173.04
yttrium	Y	39	88.90585
zinc	Zn	30	65.39
zirconium	Zr	40	91.224

A value given in brackets denotes the mass number of the most stable or most common isotope. The atomic masses of most of these elements are believed to have an error no greater than ±1 in the last digit given.

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TABLE A-7 COMMON IONS

Cation	Symbol	Anion	Symbol
aluminum	Al^{3+}	**acetate**	CH_3COO^-
ammonium	NH_4^+	**bromide**	Br^-
arsenic(III)	As^{3+}	**carbonate**	CO_3^{2-}
barium	Ba^{2+}	**chlorate**	ClO_3^-
calcium	Ca^{2+}	**chloride**	Cl^-
chromium(II)	Cr^{2+}	**chlorite**	ClO_2^-
chromium(III)	Cr^{3+}	**chromate**	CrO_4^{2-}
cobalt(II)	Co^{2+}	**cyanide**	CN^-
cobalt(III)	Co^{3+}	**dichromate**	$Cr_2O_7^{2-}$
copper(I)	Cu^+	**fluoride**	F^-
copper(II)	Cu^{2+}	**hexacyanoferrate(II)**	$Fe(CN)_6^{4-}$
hydronium	H_3O^+	**hexacyanoferrate(III)**	$Fe(CN)_6^{3-}$
iron(II)	Fe^{2+}	**hydride**	H^-
iron(III)	Fe^{3+}	**hydrogen carbonate**	HCO_3^-
lead(II)	Pb^{2+}	**hydrogen sulfate**	HSO_4^-
magnesium	Mg^{2+}	**hydroxide**	OH^-
mercury(I)	Hg_2^{2+}	**hypochlorite**	ClO^-
mercury(II)	Hg^{2+}	**iodide**	I^-
nickel(II)	Ni^{2+}	**nitrate**	NO_3^-
potassium	K^+	**nitrite**	NO_2^-
silver	Ag^+	**oxide**	O^{2-}
sodium	Na^+	**perchlorate**	ClO_4^-
strontium	Sr^{2+}	**permanganate**	MnO_4^-
tin(II)	Sn^{2+}	**peroxide**	O_2^{2-}
tin(IV)	Sn^{4+}	**phosphate**	PO_4^{3-}
titanium(III)	Ti^{3+}	**sulfate**	SO_4^{2-}
titanium(IV)	Ti^{4+}	**sulfide**	S^{2-}
zinc	Zn^{2+}	**sulfite**	SO_3^{2-}

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TABLE A-8 WATER-VAPOR PRESSURE

Temperature (°C)	Pressure (mm Hg)	Pressure (kPa)	Temperature (°C)	Pressure (mm Hg)	Pressure (kPa)
0.0	4.6	0.61	**23.0**	21.1	2.81
5.0	6.5	0.87	**23.5**	21.7	2.90
10.0	9.2	1.23	**24.0**	22.4	2.98
15.0	12.8	1.71	**24.5**	23.1	3.10
15.5	13.2	1.76	**25.0**	23.8	3.17
16.0	13.6	1.82	**26.0**	25.2	3.36
16.5	14.1	1.88	**27.0**	26.7	3.57
17.0	14.5	1.94	**28.0**	28.3	3.78
17.5	15.0	2.00	**29.0**	30.0	4.01
18.0	15.5	2.06	**30.0**	31.8	4.25
18.5	16.0	2.13	**35.0**	42.2	5.63
19.0	16.5	2.19	**40.0**	55.3	7.38
19.5	17.0	2.27	**50.0**	92.5	12.34
20.0	17.5	2.34	**60.0**	149.4	19.93
20.5	18.1	2.41	**70.0**	233.7	31.18
21.0	18.6	2.49	**80.0**	355.1	47.37
21.5	19.2	2.57	**90.0**	525.8	70.12
22.0	19.8	2.64	**95.0**	633.9	84.53
22.5	20.4	2.72	**100.0**	760.0	101.32

TABLE A-9 DENSITIES OF GASES AT STP

Gas	Density (g/L)
air, dry	1.293
ammonia	0.771
carbon dioxide	1.997
carbon monoxide	1.250
chlorine	3.214
dinitrogen monoxide	1.977
ethyne (acetylene)	1.165
helium	0.1785
hydrogen	0.0899
hydrogen chloride	1.639
hydrogen sulfide	1.539
methane	0.7168
nitrogen	1.2506
nitrogen monoxide (at 10°C)	1.340
oxygen	1.429
sulfur dioxide	2.927

TABLE A-10 DENSITY OF WATER

Temperature (°C)	Density (g/cm^3)
0	0.999 84
2	0.999 94
3.98 (maximum)	0.999 973
4	0.999 97
6	0.999 94
8	0.999 85
10	0.999 70
14	0.999 24
16	0.998 94
20	0.998 20
25	0.997 05
30	0.995 65
40	0.992 22
50	0.988 04
60	0.983 20
70	0.977 77
80	0.971 79
90	0.965 31
100	0.958 36

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TABLE A-11 SOLUBILITIES OF GASES IN WATER

Volume of gas (in liters) at STP that can be dissolved in 1 L of water at the temperature (°C) indicated.

Gas	0°C	10°C	20°C	60°C
air	0.029 18	0.022 84	0.018 68	0.012 16
ammonia	1130	870	680	200
carbon dioxide	1.713	1.194	0.878	0.359
carbon monoxide	0.035 37	0.028 16	0.023 19	0.014 88
chlorine	—	3.148	2.299	1.023
hydrogen	0.021 48	0.019 55	0.018 19	0.016 00
hydrogen chloride	512	475	442	339
hydrogen sulfide	4.670	3.399	2.582	1.190
methane	0.055 63	0.041 77	0.033 08	0.019 54
nitrogen*	0.023 54	0.018 61	0.015 45	0.010 23
nitrogen monoxide	0.073 81	0.057 09	0.047 06	0.029 54
oxygen	0.048 89	0.038 02	0.031 02	0.019 46
sulfur dioxide	79.789	56.647	39.374	—

*Atmospheric nitrogen–98.815% N_2, 1.185% inert gases

TABLE A-12 SOLUBILITY CHART

	acetate	bromide	carbonate	chlorate	chloride	chromate	hydroxide	iodine	nitrate	oxide	phosphate	silicate	sulfate	sulfide
aluminum	S	S	—	S	S	—	A	S	S	a	A	I	S	d
ammonium	S	S	S	S	S	S	S	S	S	—	S	—	S	S
barium	S	S	P	S	S	A	S	S	S	S	A	S	a	d
calcium	S	S	P	S	S	S	S	S	S	P	P	P	S	S
copper(II)	S	S	—	S	S	—	A	—	S	A	A	A	S	A
hydrogen	S	S	—	S	S	—	—	S	S	S	S	I	S	S
iron(II)	—	S	P	S	S	—	A	S	S	A	A	—	S	A
iron(III)	—	S	—	S	S	A	A	S	S	A	P	—	P	d
lead(II)	S	S	A	S	S	A	P	P	S	P	A	A	P	A
magnesium	S	S	P	S	S	S	A	S	S	A	P	A	S	d
manganese(II)	S	S	P	S	S	—	A	S	S	A	P	I	S	A
mercury(I)	P	A	A	S	a	P	—	A	S	A	A	—	P	I
mercury(II)	S	S	—	S	S	P	A	P	S	P	A	—	d	I
potassium	S	S	S	S	S	S	S	S	S	S	S	S	S	S
silver	P	a	A	S	a	P	—	I	S	P	A	—	P	A
sodium	S	S	S	S	S	S	S	S	S	d	S	S	S	S
strontium	S	S	P	S	S	P	S	S	S	S	A	A	P	S
tin(II)	d	S	—	S	S	A	A	S	d	A	A	—	S	A
tin(IV)	S	S	—	—	S	S	P	d	—	A	—	—	S	A
zinc	S	S	P	S	S	P	A	S	S	P	A	A	S	A

S = soluble in water. A = soluble in acids, insoluble in water. P = partially soluble in water, soluble in dilute acids.
I = insoluble in dilute acids and in water. a = slightly soluble in acids, insoluble in water. d = decomposes in water.

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TABLE A-13 SOLUBILITY OF COMPOUNDS

Solubilities are given in grams of solute that can be dissolved in 100 g of water at the temperature (°C) indicated.

Compound	Formula	0°C	20°C	60°C	100°C
aluminum sulfate	$Al_2(SO_4)_3$	31.2	36.4	59.2	89.0
ammonium chloride	NH_4Cl	29.4	37.2	55.3	77.3
ammonium nitrate	NH_4NO_3	118	192	421	871
ammonium sulfate	$(NH_4)_2SO_4$	70.6	75.4	88	103
barium carbonate	$BaCO_3$	—*	$0.0022^{18°}$	—*	0.0065
barium chloride dihydrate	$BaCl_2 \cdot 2H_2O$	31.2	35.8	46.2	59.4
barium hydroxide	$Ba(OH)_2$	1.67	3.89	20.94	$101.40^{80°}$
barium nitrate	$Ba(NO_3)_2$	4.95	9.02	20.4	34.4
barium sulfate	$BaSO_4$	—*	$0.000\ 246^{25°}$	—*	0.000 413
calcium carbonate	$CaCO_3$	—*	$0.0014^{25°}$	—*	$0.0018^{75°}$
calcium fluoride	CaF_2	$0.0016^{18°}$	$0.0017^{26°}$	—*	—*
calcium hydrogen carbonate	$Ca(HCO_3)_2$	16.15	16.60	17.50	18.40
calcium hydroxide	$Ca(OH)_2$	0.189	0.173	0.121	0.076
calcium sulfate	$CaSO_4$	—*	$0.209^{30°}$	—*	0.1619
copper(II) chloride	$CuCl_2$	68.6	73.0	96.5	120
copper(II) sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	23.1	32.0	61.8	114
lead(II) chloride	$PbCl_2$	0.67	1.00	1.94	3.20
lead(II) nitrate	$Pb(NO_3)_2$	37.5	54.3	91.6	133
lithium chloride	LiCl	69.2	83.5	98.4	128
lithium sulfate	Li_2SO_4	36.1	34.8	32.6	$30.9^{90°}$
magnesium hydroxide	$Mg(OH)_2$	—*	$0.0009^{18°}$	—*	0.004
magnesium sulfate	$MgSO_4$	22.0	33.7	54.6	68.3
mercury(I) chloride	Hg_2Cl_2	—*	$0.000\ 20^{25°}$	$0.001^{43°}$	—*
mercury(II) chloride	$HgCl_2$	3.63	6.57	16.3	61.3
potassium bromide	KBr	53.6	65.3	85.5	104
potassium chlorate	$KClO_3$	3.3	7.3	23.8	56.3
potassium chloride	KCl	28.0	34.2	45.8	56.3
potassium chromate	K_2CrO_4	56.3	63.7	70.1	$74.5^{90°}$
potassium iodide	KI	128	144	176	206
potassium nitrate	KNO_3	13.9	31.6	106	245
potassium permanganate	$KMnO_4$	2.83	6.34	22.1	—*
potassium sulfate	K_2SO_4	7.4	11.1	18.2	24.1
silver acetate	$AgC_2H_3O_2$	0.73	1.05	1.93	$2.59^{80°}$
silver chloride	AgCl	$0.000\ 089^{10°}$	—*	—*	0.0021
silver nitrate	$AgNO_3$	122	216	440	733
sodium acetate	$NaC_2H_3O_2$	36.2	46.4	139	170
sodium chlorate	$NaClO_3$	79.6	95.9	137	204
sodium chloride	NaCl	35.7	35.9	37.1	39.2
sodium nitrate	$NaNO_3$	73.0	87.6	122	180
sucrose	$C_{12}H_{22}O_{11}$	179.2	203.9	287.3	487.2

*Dashes indicate that values are not available.

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TABLE A-14 HEAT OF FORMATION

Substance	State	ΔH_f
ammonia	*g*	−45.9
ammonium chloride	*s*	−314.4
ammonium sulfate	*s*	−1180.9
barium chloride	*s*	−858.6
barium nitrate	*s*	−992.1
barium sulfate	*s*	−1473.2
benzene	*g*	+82.88
benzene	*l*	+49.080
calcium carbonate	*s*	−1207.6
calcium chloride	*s*	−795.4
calcium hydroxide	*s*	−983.2
calcium nitrate	*s*	−938.2
calcium oxide	*s*	−634.9
calcium sulfate	*s*	−1434.5
carbon (diamond)	*s*	+1.9
carbon (graphite)	*s*	0.00
carbon dioxide	*g*	−393.5
carbon monoxide	*g*	−110.5
copper(II) nitrate	*s*	−302.9
copper(II) oxide	*s*	−157.3
copper(II) sulfate	*s*	−771.4
ethane	*g*	−83.8
ethyne (acetylene)	*g*	+228.2
hydrogen (H_2)	*g*	0.00
hydrogen bromide	*g*	−36.29
hydrogen chloride	*g*	−92.3
hydrogen fluoride	*g*	−273.3
hydrogen iodide	*g*	+26.5
hydrogen oxide (water)	*g*	−241.8
hydrogen oxide (water)	*l*	−285.8
hydrogen peroxide	*g*	−136.3
hydrogen peroxide	*l*	−187.8
hydrogen sulfide	*g*	−23.9
iodine (I_2)	*s*	0.00
iodine (I_2)	*g*	+62.4
iron(II) chloride	*s*	−399.4
iron(II) oxide	*s*	−272.0
iron(III) oxide	*s*	−824.2
iron(II) sulfate	*s*	−928.4
iron(II) sulfide	*s*	−100.0
lead(II) oxide	*s*	−217.3
lead(IV) oxide	*s*	−274.5
lead(II) nitrate	*s*	−451.9
lead(I) sulfate	*s*	−919.94
lithium chloride	*s*	−408.6
lithium nitrate	*s*	−483.1
magnesium chloride	*s*	−641.5
magnesium oxide	*s*	−601.6
magnesium sulfate	*s*	−1284.9
manganese(IV) oxide	*s*	−520.0
manganese(II) sulfate	*s*	−1065.3
mercury(I) chloride	*s*	−264.2
mercury(II) chloride	*s*	−230.0
mercury(II) oxide (red)	*s*	−90.8
methane	*g*	−74.9
nitrogen dioxide	*g*	+33.2
nitrogen monoxide	*g*	+90.29
dinitrogen monoxide	*g*	+82.1
dinitrogen tetroxide	*g*	+9.2
oxygen (O_2)	*g*	0.00
ozone (O_3)	*g*	+142.7
diphosphorus pentoxide	*s*	−3009.9
potassium bromide	*s*	−393.8
potassium chloride	*s*	−436.49
potassium hydroxide	*s*	−424.58
potassium nitrate	*s*	−494.6
potassium sulfate	*s*	−1437.8
silicon dioxide (quartz)	*s*	−910.7
silver chloride	*s*	−127.01 ± 0.5
silver nitrate	*s*	−120.5
silver sulfide	*s*	−32.59
sodium bromide	*s*	−361.8
sodium chloride	*s*	−385.9
sodium hydroxide	*s*	−425.9
sodium nitrate	*s*	−467.9
sodium sulfate	*l*	−1387.1
sulfur dioxide	*g*	−296.8
sulfur trioxide	*g*	−395.7
tin(IV) chloride	*l*	−511.3
zinc nitrate	*s*	−483.7
zinc oxide	*s*	−350.5
zinc sulfate	*s*	−980.14

ΔH_f is heat of formation of the given substance from its elements. All values of ΔH_f are expressed as kJ/mol at 25°C. Negative values of ΔH_f indicate exothermic reactions. *s* = solid, *l* = liquid, *g* = gas

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TABLE A-15 PROPERTIES OF COMMON ELEMENTS

Name	Form/color at room temperature	Density (g/cm^3)†	Melting point (°C)	Boiling point (°C)	Common oxidation states
aluminum	silver metal	2.702	660.37	2467	3+
arsenic	gray metalloid	5.727^{14}	817 (28 atm)	613 *(sublimes)*	3−, 3+, 5+
barium	bluish white metal	3.51	725	1640	2+
bromine	red-brown liquid	3.119	−7.2	58.78	1−, 1+, 3+, 5+, 7+
calcium	silver metal	1.54	839 ± 2	1484	2+
carbon	diamond graphite	3.51 2.25	3500 (63.5 atm) 3652 *(sublimes)*	3930 —	2+, 4+
chlorine	green-yellow gas	3.214*	−100.98	−34.6	1−, 1+, 3+, 5+, 7+
chromium	gray metal	7.2028	1857 ± 20	2672	2+, 3+, 6+
cobalt	gray metal	8.9	1495	2870	2+, 3+
copper	red metal	8.92	1083.4 ± 0.2	2567	1+, 2+
fluorine	yellow gas	1.69‡	−219.62	−188.14	1−
germanium	gray metalloid	5.323^{25}	937.4	2830	4+
gold	yellow metal	19.31	1064.43	2808 ± 2	1+, 3+
helium	colorless gas	0.1785*	−272.2 (26 atm)	−268.9	0
hydrogen	colorless gas	0.0899*	−259.34	−252.8	1−, 1+
iodine	blue-black solid	4.93	113.5	184.35	1−, 1+, 3+, 5+, 7+
iron	silver metal	7.86	1535	2750	2+, 3+
lead	bluish white metal	11.343716	327.502	1740	2+, 4+
lithium	silver metal	0.534	180.54	1342	1+
magnesium	silver metal	1.745	648.8	1107	2+
manganese	gray-white metal	7.20	1244 ± 3	1962	2+, 3+, 4+, 6+, 7+
mercury	silver liquid metal	13.5462	−38.87	356.58	1+, 2+
neon	colorless gas	0.9002*	−248.67	−245.9	0
nickel	silver metal	8.90	1455	2730	2+, 3+
nitrogen	colorless gas	1.2506*	−209.86	−195.8	3−, 3+, 5+
oxygen	colorless gas	1.429*	−218.4	−182.962	2−
phosphorus	yellow solid	1.82	44.1	280	3−, 3+, 5+
platinum	silver metal	21.45	1772	3827 ± 100	2+, 4+
potassium	silver metal	0.86	63.25	760	1+
silicon	gray metalloid	2.33 ± 0.01	1410	2355	2+, 4+
silver	white metal	10.5	961.93	2212	1+
sodium	silver metal	0.97	97.8	882.9	1+
strontium	silver metal	2.6	769	1384	2+
sulfur	yellow solid	1.96	119.0	444.674	2−, 4+, 6+
tin	white metal	7.28	231.88	2260	2+, 4+
titanium	white metal	4.5	1660 ± 10	3287	2+, 3+, 4+
uranium	silver metal	19.05 ± 0.02^{25}	1132.3 ± 0.8	3818	3+, 4+, 6+
zinc	blue-white metal	7.14	419.58	907	2+

† Densities obtained at 20°C unless otherwise noted (superscript)
‡ Density of fluorine given in g/L at 1 atm and 15°C
* Densities of gases given in g/L at STP

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APPENDIX B

Study Skills for Chemistry
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APPENDIX B

Study Skills for Chemistry

Succeeding in Your Chemistry Class

Your success in this course will depend on your ability to apply some basic study skills to learning the material. Studying chemistry can be difficult, but you can make it easier using simple strategies for dealing with the concepts and problems. Becoming skilled in using these strategies will be your keys to success in this and many other courses.

Reading the Text

- **Read the assigned material before class** so that the class lecture makes sense. Use a dictionary to help you build and interpret vocabulary. Remember that, while reading, one of your tasks is to figure out what information is important.

  Working together with others using Paired Reading and Discussion strategies can help you decide what is important and clarify the material. (For more discussion, see Other Reading Strategies on page 916.)
- **Select a quiet setting** away from distractions so that you can concentrate on what you are reading.
- **Have a pencil and paper nearby to jot down notes and questions** you may have. Be sure to get these questions answered in class. Power Notes (see page 911) can help you organize the notes you take and prepare you for class.
- **Use the Objectives in the beginning of each section as a list of what you need to know from the section.** Teachers generally make their tests based on the text objectives or their own objectives. Using the objectives to focus your reading can make your learning more efficient.

  Using the K/W/L strategy (see page 914) can help you relate new material to what you already know and what you need to learn.

Taking Notes in Class

- **Be prepared to take notes during class.** Have your materials organized in a notebook. Separate sheets of paper can be easily lost.
- **Don't write down everything your teacher says.** Try to tell which parts of the lecture are important and which are not. Reading the text before class will help in this. You will not be able to write down everything, so you must try to write down only the important things.
- **Recopying notes later is a waste of time** and does not help you learn material for a test. Do

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it right the first time. Organize your notes as you are writing them down so that you can make sense of your notes when you review them without needing to recopy them.

▶ Reviewing Class Notes

- **Review your notes as soon as possible after class.** Write down any questions you may have about the material covered that day. Be sure to get these questions answered during the next class. You can work with friends to use strategies such as Paired Summarizing and L.I.N.K. (See page 918.)
- **Do not wait until the test to review.** By then you will have forgotten a good portion of the material.
- **Be selective about what you memorize.** You cannot memorize everything in a chapter. First of all, it is too time consuming. Second, memorizing and understanding are not the same thing. Memorizing topics as they appear in your notes or text does not guarantee that you will be able to correctly answer questions that require understanding of those topics. You should only memorize material that you understand. Concept Maps and other Reading Organizers, Sequencing/Pattern Puzzles, and Prediction Guides can help you understand key ideas and major concepts. (See pages 908, 915, and 917.)

▶ Working Problems

In addition to understanding the concepts, the ability to solve problems will be a key to your success in chemistry. You will probably spend a lot of time working problems in class and at home. The ability to solve chemistry problems is a skill, and like any skill, it requires practice.

- **Always review the Sample Problems in the chapter.** The Sample Problems in the text provide road maps for solving certain types of problems. Cover the solution while trying to work the problem yourself.
- **The problems in the Chapter Review are similar to the Sample Problems.** If you can relate an assigned problem to one of the Sample Problems in the chapter, it shows that you understand the material.
- **The four steps: Analyze, Plan, Compute, and Evaluate should be the steps you go through when working assigned problems.** These steps will allow you to organize your thoughts and help you develop your problem-solving skills.
- **Never spend more than 15 minutes trying to solve a problem.** If you have not been able to come up with a plan for the solution after 15 minutes, additional time spent will only cause you to become frustrated. What do you do? Get help! See your teacher or a classmate. Find out what it is that you do not understand.
- **Do not try to memorize the Sample Problems; spend your time trying to understand how the solution develops.** Memorizing a particular sample problem will not ensure that you understand it well enough to solve a similar problem.
- **Always look at your answer and ask yourself if it is reasonable and makes sense.** Check to be sure you have the correct units and numbers of significant figures.

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▶ Completing Homework

Your teacher will probably assign questions and problems from the Section Reviews and Chapter Reviews or assign *Modern Chemistry* Daily Homework. The purpose of these assignments is to review what you have covered in class and to see if you can use the information to answer questions or solve problems. As in reviewing class notes, do your homework as soon after class as possible while the topics are still fresh in your mind. Do not wait until late at night, when you are more likely to be tired and to become frustrated.

▶ Preparing for and Taking Exams

Reviewing for an exam

- **Don't panic and don't cram! It takes longer to learn if you are under pressure.** If you have followed the strategies listed here and reviewed along the way, studying for the exam should be less stressful.
- **When looking over your notes and concept maps, recite ideas out loud.** There are two reasons for reciting:
  1. You are hearing the information, which is effective in helping you learn.
  2. If you cannot recite the ideas, it should be a clue that you do not understand the material, and you should begin rereading or reviewing the material again.
- **Studying with a friend provides a good opportunity for recitation.** If you can explain ideas to your study partner, you know the material.

Taking an exam

- **Get plenty of rest before the exam so that you can think clearly.** If you have been awake all night studying, you are less likely to succeed than if you had gotten a full night of rest.
- **Start with the questions you know.** If you get stuck on a question, save it for later. As time passes and you work through the exam, you may recall the information you need to answer a difficult question or solve a difficult problem.

Good luck!

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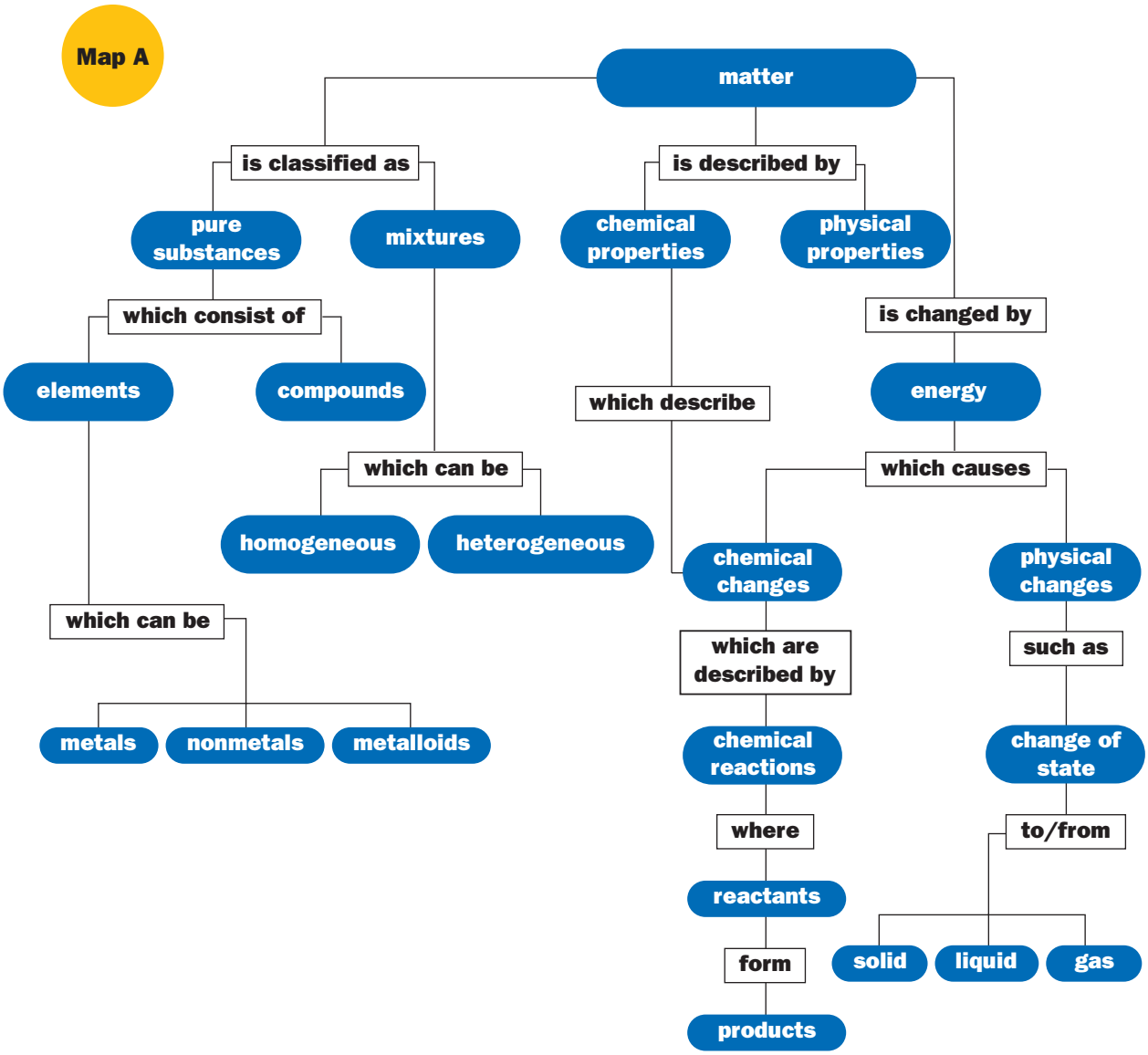
Making Concept Maps

Making concept maps can help you decide what material in a chapter is important and how to efficiently learn that material. A concept map presents key ideas, meanings, and relationships for the concepts being studied. It can be thought of as a visual road map of the chapter. Learning happens efficiently when you use concept maps because you work with only the key ideas and how they fit together.

The concept map shown as **Map A** was made from vocabulary terms in Chapter 1. Vocabulary terms are generally labels for concepts, and concepts are generally nouns. In a concept map, linking words are used to form propositions that connect concepts and give them meaning in context. For example, on the map below, "matter is described by physical properties" is a proposition.



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Back

Studies show that people are better able to remember materials presented visually. A concept map is better than an outline because you can see the relationships among many ideas. Because outlines are linear, there is no way of linking the ideas from various sections of the outline. Read through the map to become familiar with the information presented. Then look at the map in relation to all of the text pages in Chapter 1; which gives a better picture of the important concepts—the map or the full chapter?

To Make a Concept Map

1. List all the important concepts.

We'll use some of the boldfaced and italicized terms from Section 1-2.

matter	mixture
compound	pure substance
element	
homogenous mixture	
heterogeneous mixture	

- From this list, group similar concepts together. For example, one way to group these concepts would be into two groups—one that is related to mixtures and one that is related to pure substances.

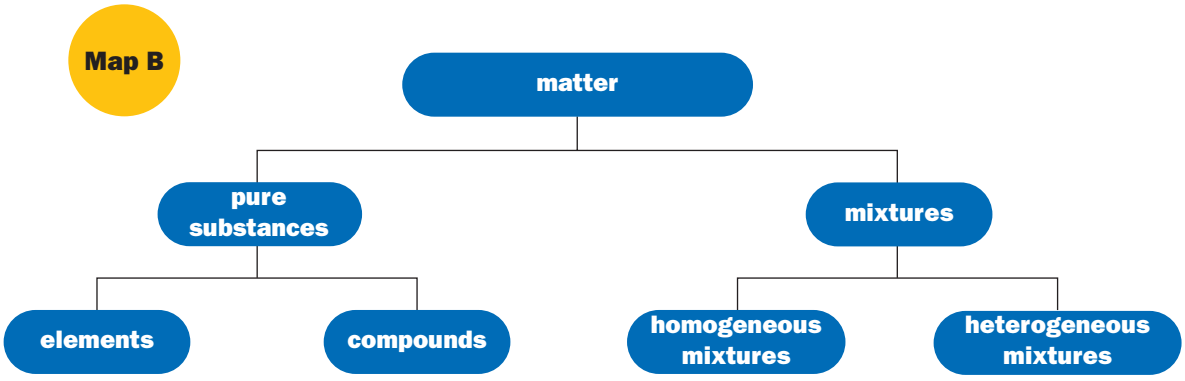
mixture	*pure substance*
heterogeneous mixture	compound
homogeneous mixture	element

2. Select a main concept for the map.

We will use *matter* as the main concept for this map.

3. Build the map by placing the concepts according to their importance under the main concept, *matter*.

One way of arranging the concepts is shown in **Map B.**



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4. Add linking words to give meaning to the arrangement of concepts.

When adding the links, be sure that each proposition makes sense. To distinguish concepts from links, place your concepts in circles, ovals, or rectangles, as shown in the maps. Then make cross-links. Cross-links are made of propositions and lines connecting concepts across the map. Links that apply in only one direction are indicated with an arrowhead. **Map C** is a finished map covering the main ideas listed in Step 1.

Making maps might seem difficult at first, but the process forces you to think about the meanings and relationships among the concepts. If you do not understand those relationships, you can get help early on.

Practice mapping by making concept maps about topics you know. For example, if you know a lot about a particular sport, such as basketball, or if you have a particular hobby, such as playing a musical instrument, you can use that topic to make a practice map. By perfecting your skills with information that you know very well, you will begin to feel more confident about making maps from the information in a chapter.

Remember, the time you devote to mapping will pay off when it is time to review for an exam.

Practice

1. Classify each of the following as either a concept or linking word(s).

a. classification _____

b. is classified as _____

c. forms _____

d. is described by _____

e. reaction _____

f. reacts with _____

g. metal _____

h. defines _____

2. Write three propositions from the information in **Map A.** _____

_____

_____

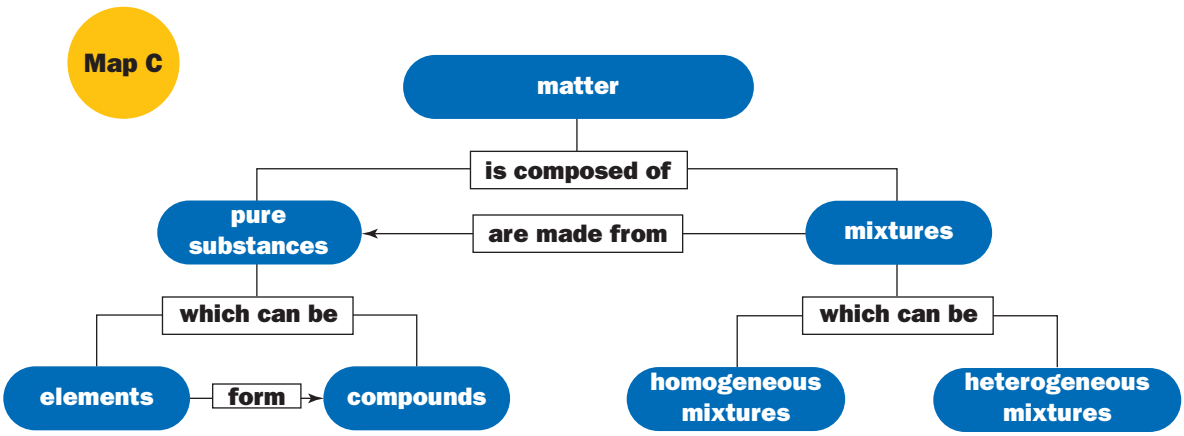
_____

3. List two cross-links shown on **Map C.**

_____

_____

_____



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Making Power Notes

Power notes help you organize the chemical concepts you are studying by distinguishing main ideas from details. Similar to outlines, power notes are linear in form and provide you with a framework of important concepts. Power notes are easier to use than outlines because their structure is simpler. Using the power notes numbering system you assign a *1* to each main idea and a *2, 3,* or *4* to each detail.

Power notes are an invaluable asset to the learning process, and they can be used frequently throughout your chemistry course. You can use power notes to organize ideas while reading your text or to restructure your class notes for studying purposes.

To learn to make power notes, practice first by using single-word concepts and a subject you are especially interested in, such as animals, sports, or movies. As you become comfortable with structuring power notes, integrate their use into your study of chemistry. For an easier transition, start with a few boldfaced or italicized terms. Later you can strengthen your notes by expanding these single-word concepts into more-detailed phrases and sentences. Use the following general format to help you structure your power notes.

Power 1: Main idea
Power 2: Detail or support for power 1
Power 3: Detail or support for power 2
Power 4: Detail or support for power 3

1. Pick a Power 1 word from the text.
The text you choose does not have to come straight from your chemistry textbook. You may be making power notes from your lecture notes or from an outside source. We'll use the term *atom* found in Section 3-2 of your textbook.

Power 1: Atom

2. Using the text, select some Power 2 words to support your Power 1 word.
We'll use the terms *nucleus* and *electrons,* which are two parts of an atom.

Power 1: Atom
Power 2: Nucleus
Power 2: Electrons

3. Select some Power 3 words to support your Power 2 words.
We'll use the terms *positively charged* and *negatively charged,* two terms that describe the Power 2 words.

Power 1: Atom
Power 2: Nucleus
Power 3: Positively charged
Power 2: Electrons
Power 3: Negatively charged

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4. Continue to add powers to support and detail the main idea as necessary.

There are no restrictions on how many power numbers you can use in your notes. If you have a main idea that requires a lot of support, add more powers to help you extend and organize your ideas. Be sure that words having the same power number have a similar relationship to the power above. Power 1 terms do not have to be related to each other. You can use power notes to organize the material in an entire section or chapter of your text. Doing so will provide you with an invaluable study guide for your classroom quizzes and tests.

Power 1: Atom
- **Power 2:** Nucleus
  - **Power 3:** Positively charged
  - **Power 3:** Protons
    - **Power 4:** Positively charged
  - **Power 3:** Neutrons
    - **Power 4:** No charge
- **Power 2:** Electrons
  - **Power 3:** Negatively charged

Practice

1. Use a periodic table and the power notes structure below to organize the following terms: *alkaline-earth metals, nonmetals, calcium, sodium, halogens, metals, alkali metals, chlorine, barium,* and *iodine.*

1 _____

2 _____

3 _____

2 _____

3 _____

3 _____

1 _____

2 _____

3 _____

3 _____

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Making Two-Column Notes

Two-column notes can be used to learn and review definitions of vocabulary terms, examples of multiple-step processes, or details of specific concepts. The two-column-note strategy is simple: write the term, main idea, step-by-step process, or concept in the left-hand column, and the definition, example, or detail on the right.

One strategy for using two-column notes is to organize main ideas and their details. The main ideas from your reading are written in the left-hand column of your paper and can be written as questions, key words, or a combination of both. Details describing these main ideas are then written in the right-hand column of your paper.

1. **Identify the main ideas.** The main ideas for a chapter are listed in the section objectives. However, you decide which ideas to include in your notes. For example, here are some main ideas from the objectives in Section 5-2.
   - Describe the locations in the periodic table and the general properties of the alkali metals, alkaline-earth metals, the halogens, and the noble gases.
2. **Divide a blank sheet of paper into two columns and write the main ideas in the left-hand column.** Summarize your ideas using quick phrases that are easy for you to understand and remember. Decide how many details you need for each main idea, and write that number in parentheses under the main idea.
3. **Write the detail notes in the right-hand column.** Be sure you list as many details as you designated in the main-idea column. Here are some main ideas and details from the objective in Section 5-2.

The two-column method of review is perfect whether you use it to study for a short quiz or for a test on the material in an entire chapter. Just cover the information in the right-hand column with a sheet of paper, and after reciting what you know, uncover the notes to check your answers. Then ask yourself what else you know about that topic. Linking ideas in this way will help you to gain a more complete picture of chemistry.

Main Idea	Detail Notes
• Alkali metals (4 properties)	• Group 1 • highly reactive • ns^1 electron configuration • soft, silvery
• Alkaline-earth metals (4 properties)	• Group 2 • reactive • ns^2 electron configuration • harder than alkali metals
• Halogens (3 properties)	• Group 17 • reactive • nonmetallic
• Noble gases	• Group 18 • low reactivity • stable ns^2np^6 configuration

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Using the K/W/L/ Strategy

The K/W/L strategy stands for "what I **K**now—what I **W**ant to know—what I **L**earned." You start by brainstorming about the subject matter before reading the assigned material. Relating new ideas and concepts to those you have learned previously will help you better understand and apply the new knowledge you obtain. The section objectives throughout your textbook are ideal for using the K/W/L strategy.

1. **Read the section objectives.** You may also want to scan headings, boldfaced terms, and illustrations before reading. Here are two of the objectives from Section 1-2 to use as an example.
   - Explain the gas, liquid, and solid states in terms of particles.
   - Distinguish between a mixture and a pure substance.
2. **Divide a sheet of paper into three columns, and label the columns "What I Know," "What I Want to Know," and "What I Learned."**
3. **Brainstorm about what you know about the information in the objectives, and write these ideas in the first column.** Because this chart is designed primarily to help you integrate your own knowledge with new information, it is not necessary to write complete sentences.
4. **Think about what you want to know about the information in the objectives, and write these ideas in the second column.** Include information from both the section objectives and any other objectives your teacher has given you.
5. **While reading the section or afterwards, use the third column to write down the information you learned.** While reading, pay close attention to any information about the topics you wrote in the "What I Want to Know" column. If you do not find all of the answers you are looking for, you may need to reread the section or reference a second source. Be sure to ask your teacher if you still cannot find the information after reading the section a second time.

It is also important to review your brainstormed ideas when you have completed reading the section. Compare your ideas in the first column with the information you wrote down in the third column. If you find that some of your brainstormed ideas are incorrect, cross them out. It is extremely important to identify and correct any misconceptions you had prior to reading before you begin studying for your test.

What I Know	What I Want to Know	What I Learned
• gas has no definite shape or volume • liquid has no definite shape, but has definite volume • solid has definite shape and volume • mixture is combination of substances • pure substance has only one component	• how gas, liquid, and solid states are related to particles • how mixtures and pure substances are different	• molecules in solid and liquid states are close together, but are far apart in gas state • molecules in solid state have fixed positions, but molecules in liquid and gas states can flow • mixtures are combinations of pure substances • pure substances have fixed compositions and definite properties

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Using Sequencing/Pattern Puzzles

You can use pattern puzzles to help you remember sequential information. Pattern puzzles are not just a tool for memorization. They also promote a greater understanding of a variety of chemical processes, from the steps in solving a mass-mass stoichiometry problem to the procedure for making a solution of specified molarity.

1. Write down the steps of a process in your own words. For an example, we will use the process for converting the amount of a substance in moles to mass in grams. (See Sample Problem 3-2 on page 82.) On a sheet of notebook paper, write down one step per line, and do not number the steps. Also, do not copy the process straight from your textbook.

Writing the steps in your own words promotes a more thorough understanding of the process. You may want to divide longer steps into two or three shorter steps.

- List the given and unknown information.
- Look at the periodic table to determine the molar mass of the substance.
- Write the correct conversion factor to convert moles to grams.
- Multiply the amount of substance by the conversion factor.
- Solve the equation and check your answer.

2. Cut the sheet of paper into strips with only one step per strip of paper. Shuffle the strips of paper so that they are out of sequence.

- Look at the periodic table to determine the molar mass of the substance.
- Solve the equation and check your answer.
- List the given and unknown information.
- Multiply the amount of substance by the conversion factor.
- Write the correct conversion factor to convert moles to grams.

3. Place the strips in their proper sequence. Confirm the order of the process by checking your text or your class notes.

- List the given and unknown information.
- Look at the periodic table to determine the molar mass of the substance.
- Write the correct conversion factor to convert moles to grams.
- Multiply the amount of substance by the conversion factor.
- Solve the equation and check your answer.

Pattern puzzles are especially helpful when you are studying for your chemistry tests. Before tests, use your puzzles to practice sequencing and to review the steps of chemistry processes. You and a classmate can also take turns creating your own pattern puzzles of different chemical processes and putting each other's puzzles in the correct sequence. Studying with a classmate in this manner will help make studying fun and will enable you to help each other.

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Other Reading Strategies

Brainstorming

Brainstorming is a strategy that helps you recognize and evaluate the knowledge you already have before you start reading. It works well individually or in groups. When you brainstorm, you start with a central term or idea, then quickly list all the words, phrases, and other ideas that you think are related to it.

Because there are no "right" or "wrong" answers, you can use the list as a basis for classifying terms, developing a general explanation, or speculating about new relationships. For example, you might brainstorm a list of terms related to the word *element* before you read Section 1-2. The list might include gold, metals, chemicals, silver, carbon, oxygen, and water. As you read the textbook, you might decide that some of the terms you listed are *not* elements. Later, you might use that information to help you distinguish between elements and compounds.

Building/Interpreting Vocabulary

Using a dictionary to look up the meanings of prefixes and suffixes as well as word origins and meanings helps you build your vocabulary and interpret what you read. If you know the meaning of prefixes like *kilo-* (one thousand) and *milli-* (one thousandth), you have a good idea what kilograms, kilometers, milligrams, and millimeters are and how they are different. (See page 35 for a list of SI Prefixes.)

Knowledge of prefixes, suffixes, and word origins can help you understand the meaning of new words. For example, if you know the suffix *-protic* comes from the same word as *proton,* it will help you understand what monoprotic and polyprotic acids are (see page 465).

Reading Hints

Reading hints help you identify and bookmark important charts, tables, and illustrations for easy reference. For example, you may want to use a self-adhesive note to bookmark the periodic table on pages 130–131 or on the inside back cover of your book so you can easily locate it and use it for reference as you study different aspects of chemistry and solve problems involving elements and compounds.

Interpreting Graphic Sources of Information

Charts, tables, photographs, diagrams, and other illustrations are graphic, or visual, sources of information. The labels and captions, together with the illustrations help you make connections between the words and the ideas presented in the text.

Reading Response Logs

Keeping a reading response log helps you interpret what you read and gives you a chance to express your reactions and opinions about what you have read. Draw a vertical line down the center of a piece of paper. In the left-hand column, write down or make notes about passages you read to which you have reactions, thoughts, feelings, questions, or associations. In the right-hand column, write what those reactions, thoughts, feelings, questions, or associations are. For example, you might keep a reading response log when studying about Nuclear Energy in Chapter 22.

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Other Studying Strategies

Comparing and Contrasting

Comparing and contrasting is a strategy that helps you note similarities and differences between two or more objects or events. When you determine similarities, you are comparing. When you determine differences, you are contrasting.

You can use comparing and contrasting to help you classify objects or properties, differentiate between similar concepts, and speculate about new relationships. For example, as you read Chapter 1 you might begin to make a table in which you compare and contrast metals, nonmetals, and metalloids. As you continue to learn about these substances in Chapters 4 and 5, you can add to your table, giving you a better understanding of the similarities and differences among elements.

Identifying Cause and Effect

Identifying causes and effects as you read helps you understand the material and builds logical reasoning skills. An effect is an event or the result of some action. A cause is the reason the event or action occurred. Signal words, such as *because, so, since, therefore, as a result,* and *depends on,* indicate a cause-and-effect relationship.

You can use arrows to show cause and effect. For example, you might write this cause-and-effect relationship as you read Section 10-3: At constant pressure, increase in temperature (cause) → increase in gas volume (effect).

Making a Prediction Guide

A prediction guide is a list of statements about which you express and try to justify your opinions based on your current knowledge. After reading the material, you re-evaluate your opinion in light of what you learned. Using prediction guides helps you evaluate your knowledge, identify assumptions you may have that could lead to mistaken conclusions, and form an idea of expected results.

1. **Read the statements your teacher writes on the board.** For example, look at the five statements from Dalton's theory listed on page 66 of your textbook.
2. **Decide whether you think each statement is true or false and discuss reasons why you think so.**
3. **After reading the section, re-evaluate your opinion of each statement. Discuss why your opinion changed or remained the same. Find passages in the text that account for the change of reinforcement of your opinions.** For example, you might have agreed with all five statements from Dalton's theory before reading the text. Then, after reading about atoms and subatomic particles, you might have changed your opinion about the first statement.

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Cooperative Learning Techniques

▶ Reading with a Partner

Reading with a partner is a strategy that can help you understand what you read and point out where more explanation is needed.

1. **First read the text silently by yourself. Use self-adhesive notes to mark those parts of the text that you do not understand.** For example, you might have difficulty with some of the material about quantum numbers in Section 4-2, while another student understands quantum numbers but has trouble with electron configurations in Section 4-3.
2. **Work with a partner to discuss the passages each of you marked.** Take turns listening and trying to clarify the difficult passages for each other. Together, study the related tables and illustrations and explain to each other how they relate to the text.
3. **For concepts that need further explanation, work together to formulate questions for class discussion or for your teacher to answer.**

▶ Using L.I.N.K.

The L.I.N.K. strategy stands for **L**ist, **I**nquire, **N**otes, **K**now. It is similar to the K/W/L strategy, but you work as a class or in groups.

1. **Brainstorm all the words, phrases, and ideas associated with the term your teacher provides.** Volunteers can keep track of contributions on the board or on a separate sheet of paper.
2. **Your teacher will direct you in a class or group discussion about the words and ideas listed.** Now is the time to inquire, or ask your teacher and other students for clarification of the listed ideas.
3. **At the end of the discussion, make notes about everything you can remember.** Look over your notes to see if you have left anything out.
4. **See what you now know about the given concept based on your own experience and the discussion.**

▶ Summarizing/Paired Summarizing

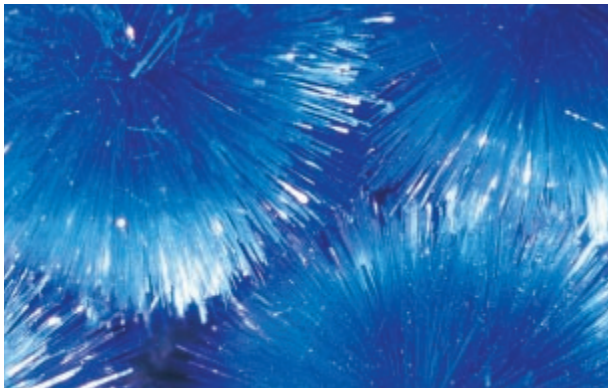
A summary is a brief statement of main ideas or important concepts. Making a summary of what you have read provides you with a way to review what you have learned, see what information needs further clarification, and helps you make connections to previously studied material.

Paired summarizing helps strengthen your ability to read, listen, and understand. It is especially useful when a section of text has several subdivisions, each dealing with different concepts, such as Section 2-3 in your textbook.

1. **First read the material silently by yourself.**
2. **Then you and your partner take turns being the "listener" and the "reteller."** The reteller summarizes the material for the listener, who does not interrupt until the reteller has finished. If necessary, the reteller may consult the text, and the listener may ask for clarification. The listener then states any inaccuracies or omissions made by the reteller.
3. **Work together to refine the summary.** Make sure the summary states the important ideas in a clear and concise manner.

▶ Discussing Ideas

Discussing ideas with a partner or in a group before you read is a strategy that can help you broaden your knowledge base and decide what concepts to focus on as you are reading. Discussing ideas after you have read a section or chapter can help you check your understanding, clarify difficult concepts, and lead you to speculate about new ideas.



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APPENDIX C

Graphing Calculator Technology

Downloading

To solve the Graphing Calculator problems in Technology & Learning sections of the Chapter Reviews, you will need to download the programs and the datasets. The application for this text, called "MODCHEM," can be found go.hrw.com.

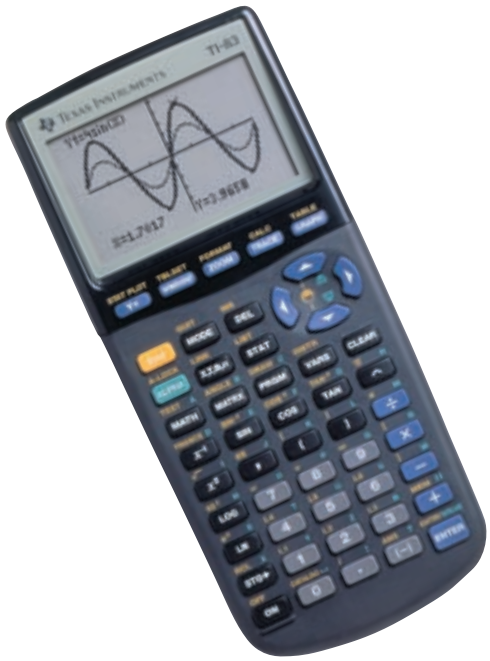
internetconnect

GO TO: go.hrw.com
KEYWORD: HC2 TI83

This Web site contains links for downloading programs and applications you will need for Technology and Learning exercises.

Note: *In order to transfer programs and applications from a computer to your calculator, you will need a TI-Graph Link cable. Programs can also be transferred directly between calculators using a unit-to-unit cable. Refer to the TI Web site or to your calculator's user's manual for instructions.*

- **If your computer does not already have TI-Graph Link software installed, click** Step 1: TI-Graph Link Software and follow the links for downloading and installing TI-Graph Link from the TI Web site.
- **Click** Step 2: ChemProg. This will load the file CHEMPROG.ZIP onto your computer. Once the file is downloaded, double-click the icon and the file will be extracted into a file called chemprog.8xg.
- **Click** Step 3: Getting Started and follow the instructions for your TI-Graph Link to load chemprog.8xg onto your TI calculator. When the file is sent to the calculator, it should expand into 17 programs. These programs should appear in the PRGM menu.



- **Download** the "MODCHEM" application from go.hrw.com.

Using the Data Sets

Once you have loaded the application, you can use it via the "apps" function on the calculator. Press the blue [APPS] button in the upper left portion of the keypad. A menu will be displayed of the applications in your calculator's memory. Look for an application titled "MODCHEM." Select it either by using the arrow keys and pressing ENTER or by using the number keys. Do this each time you choose to open the application. A title screen will appear for a few seconds, and then a menu will be displayed, listing all of the available data sets. The sets are listed by chapter and can be selected with either the arrow keys and [ENTER] or with the number keys.

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The instructions are essentially the same for every chapter. You can select the lists to be loaded by placing the cursor beside them and pressing the [ENTER] key or, if you would like to load all of the lists from that chapter at one time, you can use the arrow keys to go to the **All** menu and choose the first option **All+** and then press [ENTER]. When you have chosen all of the data sets that you need, use the arrow keys to go to the **Load** menu. The **SetUpEditor** allows you to decide where you would like the lists to be stored. **1: Add to Editor** adds the lists to the end of the List editor. By choosing [STAT] and **1: Edit…,** you can see these lists behind L_6. **2: Exchange Lists** replaces the data values in those with the sets from the application. They will be replaced in order, so if you have only one list, L_1 will be replaced, and so on. **3: No change** will not add the list to the List editor; however, by going to the List menu via [2^{nd}] [LIST], you will see the names of the data sets listed under L_6. After you have finished, choose **Load,** and the sets will be loaded into the desired location.

Graphing Data Sets

The sets for all graphing programs are listed in the order that they should be loaded—the *x*-axis data is listed before the *y*-axis data, as all the graphing programs are designed to put *x*-coordinates into L_1 and *y*-coordinates into L_2. If there are three sets, as is the case with Chapter 1, it is because one of the lists can be used with either of the others. If there are four sets, the two pairs are distinguished with the letters A and B. For example, in Chapter 10, the pressure values A are to be used with volume values A, and pressure values B are to be used with volume values B.

Before you load the sets, use the **SetUpEditor** and choose the second option, **Exchange Lists**, as L_1 and L_2 are expressly used in the graphing programs.

Calculations, Classifications (Chapter 6) and Extrapolations (Chapter 13)

These data sets must be entered somewhat manually. The programs are not designed to gain input from lists, but once you have the data in the lists, it is only a matter of referring to them.

When you run a program, the calculator will prompt you for information. When it does, press [2^{nd}] [LIST]. This will show you the names of all of the lists that you have in your list editor. Select the list with the arrow keys and press [ENTER] or with the numbers or letters associated with the list. By choosing a list, you will be taken back to the prompting screen with the list name in the place of your input. You must also include an index number. Type this number in parentheses behind the list name and press [ENTER]. If more data are needed, the calculator will prompt you. All corresponding data are listed with the same index number.

If the data are in one of the six main lists (L_1 through L_6), you can simply select the list from the keypad using the [2^{nd}] key and choosing the corresponding number. You must still add the index number in parentheses behind the name of the list.

If you do not know the index number of the datum/data you would like to use, press [STAT] and choose option **1: Edit…** Every list will be shown with all of its values. By scrolling down the list, you can find out what the index number is. At the bottom of the screen is the list name followed by a number in parentheses, an equal sign, and the value of that location in the list. The number in parentheses is the index number.

Troubleshooting

- Calculator instructions in the *Modern Chemistry* program are written for the TI-83 Plus. You may use other graphing calculators, but some of the programs and instructions may not work exactly as described.
- If you have problems loading programs or applications onto your calculator, you may need to clear programs or other data from your calculator's memory.
- Always make sure that you are downloading correct versions of the software. TI-Graph Link has different versions for Windows and for Macintosh as well as different versions for different calculators.
- If you need additional help, Texas Instruments can provide technical support at 1-800 TI-CARES.

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APPENDIX D

Problem Bank

Conversions, Section 2-2

Converting Simple SI Units

1. State the following measured quantities in the units indicated.
   - **a.** 5.2 cm of magnesium ribbon in millimeters
   - **b.** 0.049 kg of sulfur in grams
   - **c.** 1.60 mL of ethanol in microliters
   - **d.** 0.0025 g of vitamin A in micrograms
   - **e.** 0.020 kg of tin in milligrams
   - **f.** 3 kL of saline solution in liters
2. State the following measured quantities in the units indicated.
   - **a.** 150 mg of aspirin in grams
   - **b.** 2500 mL of hydrochloric acid in liters
   - **c.** 0.5 g of sodium in kilograms
   - **d.** 55 L of carbon dioxide gas in kiloliters
   - **e.** 35 mm in centimeters
   - **f.** 8740 m in kilometers
   - **g.** 209 nm in millimeters
   - **h.** 500 000 μg in kilograms
3. The greatest distance between Earth and the sun during Earth's revolution is 152 million kilometers. What is this distance in megameters?
4. How many milliliters of water will it take to fill a 2.00 L bottle that already contains 1.87 L of water?
5. A piece of copper wire is 150 cm long. How long is the wire in millimeters? How many 50 mm segments of wire can be cut from the length?
6. The ladle at an iron foundry can hold 8500 kg of molten iron; 646 metric tons of iron are needed to make rails. How many ladlefuls of iron will it take to make 646 metric tons of iron? (1 metric ton = 1000 kg)

Converting Derived SI Units

7. State the following measured quantities in the units indicated.
   - **a.** 310 000 cm^3 of concrete in cubic meters
   - **b.** 6.5 m^2 of steel sheet in square centimeters
   - **c.** 0.035 m^3 of chlorine gas in cubic centimeters
   - **d.** 0.49 cm^2 of copper in square millimeters
   - **e.** 1200 dm^3 of acetic acid solution in cubic meters
   - **f.** 87.5 mm^3 of actinium in cubic centimeters
   - **g.** 250 000 cm^2 of polyethylene sheet in square meters
8. How many palisade cells from plant leaves would fit in a volume of 1.0 cm^3 of cells if the average volume of a palisade cell is 0.0147 mm^3?

Mixed Review

9. Convert each of the following quantities to the required unit.
   - **a.** 12.75 Mm to kilometers
   - **b.** 277 cm to meters
   - **c.** 30 560 m^2 to hectares (1 ha = 10 000 m^2)
   - **d.** 81.9 cm^2 to square meters
   - **e.** 300 000 km to megameters
10. Convert each of the following quantities to the required unit.
    - **a.** 0.62 km to meters
    - **b.** 3857 g to milligrams
    - **c.** 0.0036 mL to microliters
    - **d.** 0.342 metric tons to kg (1 metric ton = 1000 kg)
    - **e.** 68.71 kL to liters
11. Convert each of the following quantities to the required unit.
    - **a.** 856 mg to kilograms
    - **b.** 1 210 000 μg to kilograms
    - **c.** 6598 μL to cubic centimeters (1 mL = 1 cm^3)
    - **d.** 80 600 nm to millimeters
    - **e.** 10.74 cm^3 to liters
12. Convert each of the following quantities to the required unit.
    - **a.** 7.93 L to cubic centimeters
    - **b.** 0.0059 km to centimeters
    - **c.** 4.19 L to cubic decimeters
    - **d.** 7.48 m^2 to square centimeters
    - **e.** 0.197 m^3 to liters
13. An automobile uses 0.05 mL of oil for each kilometer it is driven. How much oil in liters is consumed if the automobile is driven 20 000 km?
14. How many microliters are there in a volume of 370 mm^3 of cobra venom?
15. A baker uses 1.5 tsp of vanilla extract in each cake. How much vanilla extract in liters should the baker order to make 800 cakes? (1 tsp = 5 mL)
16. A person drinks eight glasses of water each day, and each glass contains 300 mL. How many liters of water will that person consume in a year? What is the mass of this volume of water in kilograms? (Assume one year has 365 days and the density of water is 1.00 kg/L.)
17. At the equator Earth rotates with a velocity of about 465 m/s.

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a. What is this velocity in kilometers per hour?
b. What is this velocity in kilometers per day?

18. A chemistry teacher needs to determine what quantity of sodium hydroxide to order. If each student will use 130 g and there are 60 students, how many kilograms of sodium hydroxide should the teacher order?

19. The teacher in item 18 also needs to order plastic tubing. If each of the 60 students needs 750 mm of tubing, what length of tubing in meters should the teacher order?

20. Convert the following to the required units.
a. 550 μL/h to milliliters per day
b. 9.00 metric tons/h to kilograms per minute
c. 3.72 L/h to cubic centimeters per minute
d. 6.12 km/h to meters per second

21. Express the following in the units indicated.
a. 2.97 kg/L as grams per cubic centimeter
b. 4128 g/dm^2 as kilograms per square centimeter
c. 5.27 g/cm^3 as kilograms per cubic decimeter
d. 6.91 kg/m^3 as milligrams per cubic millimeter

22. A gas has a density of 5.56 g/L.
a. What volume in milliliters would 4.17 g of this gas occupy?
b. What would be the mass in kilograms of 1 m^3 of this gas?

23. The average density of living matter on Earth's land areas is 0.10 g/cm^2. What mass of living matter in kilograms would occupy an area of 0.125 ha?

24. A textbook measures 250. mm long, 224 mm wide, and 50.0 mm thick. It has a mass of 2.94 kg.
a. What is the volume of the book in cubic meters?
b. What is the density of the book in grams per cubic centimeter?
c. What is the area of one cover in square meters?

25. A glass dropper delivers liquid so that 25 drops equal 1.00 mL.
a. What is the volume of one drop in milliliters?
b. How many milliliters are in 37 drops?
c. How many drops would be required to get 0.68 L?

26. Express each of the following in kilograms and grams.
a. 504 700 mg
b. 9 200 000 μg
c. 122 mg
d. 7195 cg

27. Express each of the following in liters and milliliters.
a. 582 cm^3
b. 0.0025 m^3
c. 1.18 dm^3
d. 32 900 μL

28. Express each of the following in grams per liter and kilograms per cubic meter.
a. 1.37 g/cm^3
b. 0.692 kg/dm^3
c. 5.2 kg/L
d. 38 000 g/m^3
e. 5.79 mg/mm^3
f. 1.1 μg/mL

29. An industrial chemical reaction is run for 30.0 h and produces 648.0 kg of product. What is the average rate of product production in the stated units?
a. grams per minute
b. kilograms per day
c. milligrams per millisecond

30. What is the speed of a car in meters per second when it is moving at 100. km/h?

31. A heater gives off heat at a rate of 330 kJ/min. What is the rate of heat output in kilocalories per hour? (1 cal = 4.184 J)

32. The instructions on a package of fertilizer tell you to apply it at the rate of 62 g/m^2. How much fertilizer in kilograms would you need to apply to 1.0 ha? (1 ha = 10 000 m^2)

33. A water tank leaks water at the rate of 3.9 mL/h. If the tank is not repaired, what volume of water in liters will it leak in a year? Show your setup for solving this. Hint: Use one conversion factor to convert hours to days and another to convert days to years, and assume that one year has 365 days.

34. A nurse plans to give flu injections of 50 μL each from a bottle containing 2.0 mL of vaccine. How many doses are in the bottle?

Significant Figures, Section 2-3

35. Determine the number of significant figures in the following measurements.
a. 640 cm^3
b. 200.0 mL
c. 0.5200 g
d. 1.005 kg
e. 10 000 L
f. 20.900 cm
g. 0.000 000 56 g/L
h. 0.040 02 kg/m^3
i. 790 001 cm^2
j. 665.000 kg•m/s^2

36. Perform the following calculations, and express the result in the correct units and number of significant figures.
a. 47.0 m ÷ 2.2 s
b. 140 cm × 35 cm
c. 5.88 kg ÷ 200 m^3
d. 0.00 50 m^2 × 0.042 m
e. 300.3 L ÷ 180. s
f. 33.00 cm^2 × 2.70 cm
g. 35 000 kJ ÷ 0.250 min

37. Perform the following calculations and express the results in the correct units and number of significant figures.
a. 22.0 m + 5.28 m + 15.5 m
b. 0.042 kg + 1.229 kg + 0.502 kg
c. 170 cm^2 + 3.5 cm^2 − 28 cm^2
d. 0.003 L + 0.0048 L + 0.100 L
e. 24.50 dL + 4.30 dL + 10.2 dL
f. 3200 mg + 325 mg − 688 mg
g. 14 000 kg + 8000 kg + 590 kg

Mixed Review

38. Determine the number of significant figures in the following measurements.
a. 0.0120 m
b. 100.5 mL
c. 101 g
d. 350 cm^2
e. 0.97 km
f. 1000 kg
g. 180. mm
h. 0.4936 L
i. 0.020 700 s

39. Round the following quantities to the specified number of significant figures.
a. 5 487 129 m to three significant figures
b. 0.013 479 265 mL to six significant figures

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c. 31 947.972 cm^2 to four significant figures
d. 192.6739 m^2 to five significant figures
e. 786.9164 cm to two significant figures
f. 389 277 600 J to six significant figures
g. 225 834.762 cm^3 to seven significant figures

40. Perform the following calculations, and express the answer in the correct units and number of significant figures.
a. 651 cm × 75 cm
b. 7.835 kg ÷ 2.5 L
c. 14.75 L ÷ 1.20 s
d. 360 cm × 51 cm × 9.07 cm
e. 5.18 m × 0.77 m × 10.22 m
f. 34.95 g ÷ 11.169 cm^3

41. Perform the following calculations, and express the answer in the correct units and number of significant figures.
a. 7.945 J + 82.3 J − 0.02 J
b. 0.0012 m − 0.000 45 m − 0.000 11 m
c. 500 g + 432 g + 2 g
d. 31.2 kPa + 0.0035 kPa − 0.147 kPa
e. 312 dL − 31.2 dL − 3.12 dL
f. 1701 kg + 50 kg + 43 kg

42. A rectangle measures 87.59 cm by 35.1 mm. Express its area with the proper number of significant figures in the specified unit.
a. in cm^2
b. in mm^2
c. in m^2

43. A box measures 900. mm by 31.5 mm by 6.3 cm. State its volume with the proper number of significant figures in the specified unit.
a. in cm^3
b. in m^3
c. in mm^3

44. A 125 mL sample of liquid has a mass of 0.16 kg. What is the density of the liquid in the following measurements?
a. kg/m^3
b. g/mL
c. kg/dm^3

45. Perform the following calculations, and express the results in the correct units and with the proper number of significant figures.
a. 13.75 mm × 10.1 mm × 0.91 mm
b. 89.4 cm^2 × 4.8 cm
c. 14.9 m^3 ÷ 3.0 m^2
d. 6.975 m × 30 m × 21.5 m

46. What is the volume of a region of space that measures 752 m × 319 m × 110 m? Give your answer in the correct unit and with the proper number of significant figures.

47. Perform the following calculations, and express the results in the correct units and with the proper number of significant figures.
a. 7.382 g + 1.21 g + 4.7923 g
b. 51.3 mg + 83 mg − 34.2 mg
c. 0.007 L − 0.0037 L + 0.012 L
d. 253.05 cm^2 + 33.9 cm^2 + 28 cm^2
e. 14.77 kg + 0.086 kg − 0.391 kg
f. 319 mL + 13.75 mL + 20. mL

48. A container measures 30.5 mm × 202 mm × 153 mm. When it is full of a liquid, it has a mass of 1.33 kg. When it is empty, it has a mass of 0.30 kg. What is the density of the liquid in kilograms per liter?

49. If 7.76 km of wire has a mass of 3.3 kg, what is the mass of the wire in g/m? What length in meters would have a mass of 1.0 g?

50. A container of plant food recommends an application rate of 52 kg/ha. If the container holds 10 kg of plant food, how many square meters will it cover? (1 ha = 10 000 m^2)

51. A chemical process produces 974 550 kJ of heat in 37.0 min. What is the rate in kilojoules per minute? What is the rate in kilojoules per second?

52. A water pipe fills a container that measures 189 cm × 307 cm × 272 cm in 97 s.
a. What is the volume of the container in cubic meters?
b. What is the rate of flow in the pipe in liters per minute?
c. What is the rate of flow in cubic meters per hour?

53. Perform the following calculations, and express the results in the correct units and with the proper number of significant figures. Note, in problems with multiple steps, it is better to perform the entire calculation and then round to significant figures.
a. (0.054 kg + 1.33 kg) × 5.4 m^2
b. 67.35 cm^2 ÷ (1.401 cm − 0.399 cm)
c. 4.198 kg × (1019 m^2 − 40 m^2) ÷ (54.2 s × 31.3 s)
d. 3.14159 m × (4.17 m + 2.150 m)
e. 690 000 m ÷ (5.022 h − 4.31 h)
f. (6.23 cm + 3.111 cm − 0.05 cm) × 14.99 cm

Scientific Notation, Section 2-3

Converting Quantities to Scientific Notation

54. Express the following quantities in scientific notation.
a. 8 800 000 000 m
b. 0.0015 kg
c. 0.000 000 000 06 kg/m^3
d. 8 002 000 Hz
e. 0.009 003 A
f. 70 000 000 000 000 000 km
g. 6028 L
h. 0.2105 g
i. 600 005 000 kJ/h
j. 33.8 m^2

Calculating with Quantities in Scientific Notation

55. Carry out the following calculations. Express the results in scientific notation and with the correct number of significant figures.
a. 4.74×10^4 km + 7.71×10^3 km + 1.05×10^3 km
b. 2.75×10^{-4} m + 8.03×10^{-5} m + 2.122×10^{-3} m
c. 4.0×10^{-5} m^3 + 6.85×10^{-6} m^3 − 1.05×10^{-5} m^3
d. 3.15×10^2 mg + 3.15×10^3 mg + 3.15×10^4 mg
e. 3.01×10^{22} atoms + 1.19×10^{23} atoms + 9.80×10^{21} atoms
f. 6.85×10^7 nm + 4.0229×10^8 nm − 8.38×10^6 nm

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56. Carry out the following computations, and express the result in scientific notation.
a. 7.20×10^3 cm $\times$ 8.08×10^3 cm
b. 3.7×10^4 mm $\times$ 6.6×10^4 mm $\times$ 9.89×10^3 mm
c. 8.27×10^2 m $\times$ 2.5×10^{-3} m $\times$ 3.00×10^{-4} m
d. 4.44×10^{-35} m $\times$ 5.55×10^{19} m $\times$ 7.69×10^{-12} kg
e. 6.55×10^4 dm $\times$ 7.89×10^9 dm $\times$ 4.01893×10^5 dm

57. Carry out the following computations, and express the result in scientific notation.
a. 2.290×10^7 cm $\div$ 4.33×10^3 s
b. 1.788×10^{-5} L $\div$ 7.111×10^{-3} m^2
c. 5.515×10^4 L $\div$ 6.04×10^3 km
d. 3.29×10^{-4} km $\div$ 1.48×10^{-2} min
e. 4.73×10^{-4} g $\div$ (2.08×10^{-3} km $\times$ 5.60×10^{-4} km)

Mixed Review

58. Express the following quantities in scientific notation.
a. 158 000 km
b. 0.000 009 782 L
c. 837 100 000 cm^3
d. 6 500 000 000 mm^2
e. 0.005 93 g
f. 0.000 000 006 13 m
g. 12 552 000 J
h. 0.000 008 004 g/L
i. 0.010 995 kg
j. 1 050 000 000 Hz

59. Perform the following calculations, and express the result in scientific notation with the correct number of significant figures.
a. 2.48×10^2 kg + 9.17×10^3 kg + 7.2×10^1 kg
b. 4.07×10^{-5} mg + 3.966×10^{-4} mg + 7.1×10^{-2} mg
c. 1.39×10^4 m^3 + 6.52×10^2 m^3 − 4.8×10^3 m^3
d. 7.70×10^{-9} m − 3.95×10^{-8} m + 1.88×10^{-7} m
e. 1.111×10^5 J + 5.82×10^4 J + 3.01×10^6 J
f. 9.81×10^{27} molecules + 3.18×10^{25} molecules − 2.09×10^{26} molecules
g. 1.36×10^7 cm + 3.456×10^6 cm − 1.01×10^7 cm + 5.122×10^5 cm

60. Perform the following computations, and express the result in scientific notation with the correct number of significant figures.
a. 1.54×10^{-1} L $\div$ 2.36×10^{-4} s
b. 3.890×10^4 mm $\times$ 4.71×10^2 mm^2
c. 9.571×10^3 kg $\div$ 3.82×10^{-1} m^2
d. 8.33×10^3 km $\div$ 1.97×10^2 s
e. 9.36×10^2 m $\times$ 3.82×10^3 m $\times$ 9.01×10^{-1} m
f. 6.377×10^4 J $\div$ 7.35×10^{-3} s

61. Your electric company charges you for the electric energy you use, measured in kilowatt-hours (kWh). One kWh is equivalent to 3 600 000 J. Express this quantity in scientific notation.

62. The pressure in the deepest part of the ocean is 11 200 000 Pa. Express this pressure in scientific notation.

63. Convert 1.5 km to millimeters, and express the result in scientific notation.

64. Light travels at a speed of about 300 000 km/s.
a. Express this value in scientific notation.
b. Convert this value to meters per hour.
c. What distance in centimeters does light travel in 1 μs?

65. There are 7.11×10^{24} molecules in 100.0 cm^3 of a certain substance.
a. What is the number of molecules in 1.09 cm^3 of the substance?
b. What would be the number of molecules in 2.24×10^4 cm^3 of the substance?
c. What number of molecules are in 9.01×10^{-6} cm^3 of the substance?

66. The number of transistors on a particular integrated circuit is 3 578 000, and the integrated circuit measures 9.5 mm $\times$ 8.2 mm.
a. What is the area occupied by each transistor?
b. Using your answer from (a), how many transistors could be formed on a silicon sheet that measures 353 mm $\times$ 265 mm?

67. A solution has 0.0501 g of a substance in 1.00 L. Express this concentration in grams per microliter.

68. Cesium atoms are the largest of the naturally occurring elements. They have a diameter of 5.30×10^{-10} m. Calculate the number of cesium atoms that would have to be lined up to give a row of cesium atoms 2.54 cm (1 in.) long.

69. The neutron has a volume of approximately 1.4×10^{-44} m^3 and a mass of 1.675×10^{-24} g. Calculate the density of the neutron in g/m^3. What is the mass of 1.0 cm^3 of neutrons in kilograms?

70. The pits in a compact disc are some of the smallest things ever mass-produced mechanically by humans. These pits represent the 1s and 0s of digital information on a compact disc. These pits are only 1.6×10^{-8} m deep (1/4 the wavelength of red laser light). How many of these pits would have to be stacked on top of each other to make a hole 0.305 m deep?

71. 22 400 mL of oxygen gas contains 6.022×10^{23} oxygen molecules at 0°C and standard atmospheric pressure.
a. How many oxygen molecules are in 0.100 mL of gas?
b. How many oxygen molecules are in 1.00 L of gas?
c. What is the average space in milliliters occupied by one oxygen molecule?

72. The mass of the atmosphere is calculated to be 5.136×10^{18} kg, and there are 6 500 000 000 people living on Earth. Calculate the following values.
a. The mass of atmosphere in kilograms per person.
b. The mass of atmosphere in metric tons per person.
c. If the number of people increases to 9 500 000 000, what is the mass in kilograms per person?

73. The mass of the sun is 1.989×10^{30} kg, and the mass of Earth is 5.974×10^{24} kilograms. How many Earths would be needed to equal the mass of the sun?

74. A new landfill has dimensions of 2.3 km $\times$ 1.4 km $\times$ 0.15 km.

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a. What is the volume in cubic kilometer?
b. What is the volume in cubic meters?
c. If 250 000 000 objects averaging 0.060 m^3 each are placed into the landfill each year, how many years will it take to fill the landfill?

75. A dietary calorie (C) is exactly equal to 1000 cal. If your daily intake of food gives you 2400 C, what is your intake in joules per day? (1 cal = 4.184 J)

Four Steps for Solving Quantitative Problems, Section 2-3

76. Gasoline has a density of 0.73 g/cm^3. How many liters of gasoline would be required to increase the mass of an automobile from 1271 kg to 1305 kg?

77. A swimming pool measures 9.0 m long by 3.5 m wide by 1.75 m deep. What mass of water in metric tons (1 metric ton = 1000 kg) does the pool contain when filled? The density of the water in the pool is 0.997 g/cm^3.

78. A tightly packed box of crackers contains 250 g of crackers and measures 7.0 cm × 17.0 cm × 19.0 cm. What is the average density in kilograms per liter of the crackers in the package? Assume that the unused volume is negligible.

Mixed Review

Solve these problems by using the Four Steps for Solving Quantitative Problems.

79. The aluminum foil on a certain roll has a total area of 18.5 m^2 and a mass of 1275 g. Using a density of 2.7 g per cubic centimeter for aluminum, determine the thickness in millimeters of the aluminum foil.

80. If a liquid has a density of 1.17 g/cm^3, how many liters of the liquid have a mass of 3.75 kg?

81. A stack of 500 sheets of paper measuring 28 cm × 21 cm is 44.5 mm high and has a mass of 2090 g. What is the density of the paper in grams per cubic centimeter?

82. A triangular-shaped piece of a metal has a mass of 6.58 g. The triangle is 0.560 mm thick and measures 36.4 mm on the base and 30.1 mm in height. What is the density of the metal in grams per cubic centimeter?

83. A packing crate measures 0.40 m × 0.40 m × 0.25 m. You must fill the crate with boxes of cookies that each measure 22.0 cm × 12.0 cm × 5.0 cm. How many boxes of cookies can fit into the crate?

84. Calculate the unknown quantities in the following table. Use the following relationships for volumes of the various shapes.

Volume of a cube = $l \times l \times l$
Volume of a rectangle = $l \times w \times h$
Volume of a sphere = $4/3\pi r^3$
Volume of a cylinder = $\pi r^2 \times h$

D	*m*	*V*	*Shape*	*Dimensions*
a. 2.27 g/cm^3	3.93 kg	? L	cube	? m × ? m × ? m
b. 1.85 g/cm^3	? g	? cm^3	rectangle	33 mm × 21 mm × 7.2 mm
c. 3.21 g/L	? kg	? dm^3	sphere	3.30 m diameter
d. ? g/cm^3	497 g	? m^3	cylinder	7.5 cm diameter × 12 cm
e. 0.92 g/cm^3	? kg	? cm^3	rectangle	3.5 m × 1.2 m × 0.65 m

85. When a sample of a metal alloy that has a mass of 9.65 g is placed into a graduated cylinder containing water, the volume reading in the cylinder increases from 16.0 mL to 19.5 mL. What is the density of the alloy sample in grams per cubic centimeter?

86. Pure gold can be made into extremely thin sheets called gold leaf. Suppose that 50. kg of gold is made into gold leaf having an area of 3620 m^2. The density of gold is 19.3 g/cm^3.
a. How thick in micrometers is the gold leaf?
b. A gold atom has a radius of 1.44×10^{-10} m. How many atoms thick is the gold leaf?

87. A chemical plant process requires that a cylindrical reaction tank be filled with a certain liquid in 238 s. The tank is 1.2 m in diameter and 4.6 m high. What flow rate in liters per minute is required to fill the reaction tank in the specified time?

88. The radioactive decay of 2.8 g of plutonium-238 generates 1.0 joule of heat every second. Plutonium has a density of 19.86 g/cm^3. How many calories (1 cal = 4.184 J) of heat will a rectangular piece of plutonium that is 4.5 cm × 3.05 cm × 15 cm generate per hour?

89. The mass of Earth is 5.974×10^{24} kg. Assume that Earth is a sphere of diameter 1.28×10^4 km and calculate the average density of Earth in grams per cubic centimeter.

90. What volume of magnesium in cubic centimeters would have the same mass as 1.82 dm^3 of platinum? The density of magnesium is 1.74 g/cm^3, and the density of platinum is 21.45 g/cm^3.

91. A roll of transparent tape has 66 m of tape on it. If an average of 5.0 cm of tape is needed each time the tape is used, how many uses can you get from a case of tape containing 24 rolls?

92. An automobile can travel 38 km on 4.0 L of gasoline. If the automobile is driven 75% of the days in a year and the average distance traveled each day is 86 km, how many liters of gasoline will be consumed in one year (assume the year has 365 days)?

93. A hose delivers water to a swimming pool that measures 9.0 m long by 3.5 m wide by 1.75 m deep. It requires 97 h to fill the pool. At what rate in liters per minute will the hose fill the pool?

94. Automobile batteries are filled with a solution of sulfuric acid, which has a density of 1.285 g/cm^3. The solution used to fill the battery is 38% (by mass) sulfuric

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acid. How many grams of sulfuric acid are present in 500 mL of battery acid?

Mole Concept, Sections 3-3; 7-3

Problems Involving Atoms and Elements

95. Calculate the number of moles in each of the following masses.
- **a.** 64.1 g of aluminum
- **b.** 28.1 g of silicon
- **c.** 0.255 g of sulfur
- **d.** 850.5 g of zinc

96. Calculate the mass of each of the following amounts.
- **a.** 1.22 mol sodium
- **b.** 14.5 mol copper
- **c.** 0.275 mol mercury
- **d.** 9.37×10^{-3} mol magnesium

97. Calculate the amount in moles in each of the following quantities.
- **a.** 3.01×10^{23} atoms of rubidium
- **b.** 8.08×10^{22} atoms of krypton
- **c.** 5 700 000 000 atoms of lead
- **d.** 2.997×10^{25} atoms of vanadium

98. Calculate the number of atoms in each of the following amounts.
- **a.** 1.004 mol bismuth
- **b.** 2.5 mol manganese
- **c.** 0.000 0002 mol helium
- **d.** 32.6 mol strontium

99. Calculate the number of atoms in each of the following masses.
- **a.** 54.0 g of aluminum
- **b.** 69.45 g of lanthanum
- **c.** 0.697 g of gallium
- **d.** 0.000 000 020 g beryllium

100. Calculate the mass of the following numbers of atoms.
- **a.** 6.022×10^{24} atoms of tantalum
- **b.** 3.01×10^{21} atoms of cobalt
- **c.** 1.506×10^{24} atoms of argon
- **d.** 1.20×10^{25} atoms of helium

Problems Involving Molecules, Formula Units, and Ions

101. Calculate the number of moles in each of the following masses.
- **a.** 3.00 g of boron tribromide, BBr_3
- **b.** 0.472 g of sodium fluoride, NaF
- **c.** 7.50×10^2 g of methanol, CH_3OH
- **d.** 50.0 g of calcium chlorate, $Ca(ClO_3)_2$

102. Determine the mass of each of the following amounts.
- **a.** 1.366 mol of NH_3
- **b.** 0.120 mol of glucose, $C_6H_{12}O_6$
- **c.** 6.94 mol barium chloride, $BaCl_2$
- **d.** 0.005 mol of propane, C_3H_8

103. Calculate the number of molecules in each of the following amounts.
- **a.** 4.99 mol of methane, CH_4
- **b.** 0.005 20 mol of nitrogen gas, N_2
- **c.** 1.05 mol of phosphorus trichloride, PCl_3
- **d.** 3.5×10^{-5} mol of vitamin C, ascorbic acid, $C_6H_8O_6$

104. Calculate the number of formula units in the following amounts.
- **a.** 1.25 mol of potassium bromide, KBr
- **b.** 5.00 mol of magnesium chloride, $MgCl_2$
- **c.** 0.025 mol of sodium carbonate, Na_2CO_3
- **d.** 6.82×10^{-6} mol of lead(II) nitrate, $Pb(NO_3)_2$

105. Calculate the amount in moles of the following numbers of molecules or formula units.
- **a.** 3.34×10^{34} formula units of $Cu(OH)_2$
- **b.** 1.17×10^{16} molecules of H_2S
- **c.** 5.47×10^{21} formula units of nickel(II) sulfate, $NiSO_4$
- **d.** 7.66×10^{19} molecules of hydrogen peroxide, H_2O_2

106. Calculate the mass of each of the following quantities.
- **a.** 2.41×10^{24} molecules of hydrogen, H_2
- **b.** 5.00×10^{21} formula units of aluminum hydroxide, $Al(OH)_3$
- **c.** 8.25×10^{22} molecules of bromine pentafluoride, BrF_5
- **d.** 1.20×10^{23} formula units of sodium oxalate, $Na_2C_2O_4$

107. Calculate the number of molecules or formula units in each of the following masses.
- **a.** 22.9 g of sodium sulfide, Na_2S
- **b.** 0.272 g of nickel(II) nitrate, $Ni(NO_3)_2$
- **c.** 260 mg of acrylonitrile, CH_2CHCN

Mixed Review

108. Calculate the number of moles in each of the following masses.
- **a.** 0.039 g of palladium
- **b.** 8200 g of iron
- **c.** 0.0073 kg of tantalum
- **d.** 0.006 55 g of antimony
- **e.** 5.64 kg of barium
- **f.** 3.37×10^{-6} g of molybdenum

109. Calculate the mass in grams of each of the following amounts.
- **a.** 1.002 mol of chromium
- **b.** 550 mol of aluminum
- **c.** 4.08×10^{-8} mol of neon
- **d.** 7 mol of titanium
- **e.** 0.0086 mol of xenon
- **f.** 3.29×10^4 mol of lithium

110. Calculate the number of atoms in each of the following amounts.
- **a.** 17.0 mol of germanium
- **b.** 0.6144 mol of copper
- **c.** 3.02 mol of tin
- **d.** 2.0×10^6 mol of carbon
- **e.** 0.0019 mol of zirconium
- **f.** 3.227×10^{-10} mol of potassium

111. Calculate the number of moles in each of the following quantities.
- **a.** 6.022×10^{24} atoms of cobalt
- **b.** 1.06×10^{23} atoms of tungsten
- **c.** 3.008×10^{19} atoms of silver

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d. 950 000 000 atoms of plutonium
e. 4.61×10^{17} atoms of radon
f. 8 trillion atoms of cerium

112. Calculate the number of atoms in each of the following masses.
a. 0.0082 g of gold
b. 812 g of molybdenum
c. 2.00×10^{2} mg of americium
d. 10.09 kg of neon
e. 0.705 mg of bismuth
f. 37 μg of uranium

113. Calculate the mass of each of the following.
a. 8.22×10^{23} atoms of rubidium
b. 4.05 Avogadro's constants of manganese atoms
c. 9.96×10^{26} atoms of tellurium
d. 0.000 025 Avogadro's constants of rhodium atoms
e. 88 300 000 000 000 atoms of radium
f. 2.94×10^{17} atoms of hafnium

114. Calculate the number of moles in each of the following masses.
a. 45.0 g of acetic acid, CH_3COOH
b. 7.04 g of lead(II) nitrate, $Pb(NO_3)_2$
c. 5000 kg of iron(III) oxide, Fe_2O_3
d. 12.0 mg of ethylamine, $C_2H_5NH_2$
e. 0.003 22 g of stearic acid, $C_{17}H_{35}COOH$
f. 50.0 kg of ammonium sulfate, $(NH_4)_2SO_4$

115. Calculate the mass of each of the following amounts.
a. 3.00 mol of selenium oxybromide, $SeOBr_2$
b. 488 mol of calcium carbonate, $CaCO_3$
c. 0.0091 mol of retinoic acid, $C_{20}H_{28}O_2$
d. 6.00×10^{-8} mol of nicotine, $C_{10}H_{14}N_2$
e. 2.50 mol of strontium nitrate, $Sr(NO_3)_2$
f. 3.50×10^{-6} mol of uranium hexafluoride, UF_6

116. Calculate the number of molecules or formula units in each of the following amounts.
a. 4.27 mol of tungsten(VI) oxide, WO_3
b. 0.003 00 mol of strontium nitrate, $Sr(NO_3)_2$
c. 72.5 mol of toluene, $C_6H_5CH_3$
d. 5.11×10^{-7} mol of α-tocopherol (vitamin E), $C_{29}H_{50}O_2$
e. 1500 mol of hydrazine, N_2H_4
f. 0.989 mol of nitrobenzene $C_6H_5NO_2$

117. Calculate the number of molecules or formula units in each of the following masses.
a. 285 g of iron(III) phosphate, $FePO_4$
b. 0.0084 g of C_5H_5N
c. 85 mg of 2-methyl-1-propanol, $(CH_3)_2CHCH_2OH$
d. 4.6×10^{-4} g of mercury(II) acetate, $Hg(C_2H_3O_2)_2$
e. 0.0067 g of lithium carbonate, Li_2CO_3

118. Calculate the mass of each of the following quantities.
a. 8.39×10^{23} molecules of fluorine, F_2
b. 6.82×10^{24} formula units of beryllium sulfate, $BeSO_4$
c. 7.004×10^{26} molecules of chloroform, $CHCl_3$
d. 31 billion formula units of chromium(III) formate, $Cr(CHO_2)_3$
e. 6.3×10^{18} molecules of nitric acid, HNO_3
f. 8.37×10^{25} molecules of freon 114, $C_2Cl_2F_4$

119. Precious metals are commonly measured in troy ounces. A troy ounce is equivalent to 31.1 g. How many moles are in a troy ounce of gold? How many moles are in a troy ounce of platinum? of silver?

120. A chemist needs 22.0 g of phenol, C_6H_5OH, for an experiment. How many moles of phenol is this?

121. A student needs 0.015 mol of iodine crystals, I_2, for an experiment. What mass of iodine crystals should the student obtain?

122. The weight of a diamond is given in carats. One carat is equivalent to 200. mg. A pure diamond is made up entirely of carbon atoms. How many carbon atoms make up a 1.00 carat diamond?

123. 8.00 g of calcium chloride, $CaCl_2$, is dissolved in 1.000 kg of water.
a. How many moles of $CaCl_2$ are in solution? How many moles of water are present?
b. Assume that the ionic compound, $CaCl_2$, separates completely into Ca^{2+} and Cl^- ions when it dissolves in water. How many moles of each ion are present in the solution?

124. How many moles are in each of the following masses?
a. 453.6 g (1.000 pound) of sucrose (table sugar), $C_{12}H_{22}O_{11}$
b. 1.000 pound of table salt, NaCl

125. When the ionic compound NH_4Cl dissolves in water, it breaks into one ammonium ion, NH_4^+, and one chloride ion, Cl^-. If you dissolved 10.7 g of NH_4Cl in water, how many moles of ions would be in solution?

126. What is the total amount in moles of atoms in a jar that contains 2.41×10^{24} atoms of chromium, 1.51×10^{23} atoms of nickel, and 3.01×10^{23} atoms of copper?

127. The density of liquid water is 0.997 g/mL at 25°C.
a. Calculate the mass of 250.0 mL (about a cupful) of water.
b. How many moles of water are in 250.0 mL of water? Hint: Use the result of (a).
c. Calculate the volume that would be occupied by 2.000 mol of water at 25°C.
d. What mass of water is 2.000 mol of water?

128. An Avogadro's constant (1 mol) of sugar molecules has a mass of 342 g, but an Avogadro's constant (1 mol) of water molecules has a mass of only 18 g. Explain why there is such a difference between the mass of 1 mol of sugar and the mass of 1 mol of water.

129. Calculate the mass of aluminum that would have the same number of atoms as 6.35 g of cadmium.

130. A chemist weighs a steel cylinder of compressed oxygen, O_2, and finds that it has a mass of 1027.8 g. After some of the oxygen is used in an experiment, the cylinder has a mass of 1023.2 g. How many moles of oxygen gas are used in the experiment?

131. Suppose that you could decompose 0.250 mol of Ag_2S into its elements.
a. How many moles of silver would you have? How many moles of sulfur would you have?
b. How many moles of Ag_2S are there in 38.8 g of Ag_2S? How many moles of silver and sulfur would be produced from this amount of Ag_2S?
c. Calculate the masses of silver and sulfur produced in (b).

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Percentage Composition, Section 7-3

132. Determine the percentage composition of each of the following compounds.
- **a.** sodium oxalate, $Na_2C_2O_4$
- **b.** ethanol, C_2H_5OH
- **c.** aluminum oxide, Al_2O_3
- **d.** potassium sulfate, K_2SO_4

133. Suppose that a laboratory analysis of white powder showed 42.59% Na, 12.02% C, and 44.99% oxygen. Would you report that the compound is sodium oxalate or sodium carbonate? (Use 43.38% Na, 11.33% C, and 45.29% O for sodium carbonate, and 34.31% Na, 17.93% C, and 47.76% O for sodium oxalate.)

134. Calculate the mass of the given element in each of the following compounds.
- **a.** bromine in 50.0 g potassium bromide, KBr
- **b.** chromium in 1.00 kg sodium dichromate, $Na_2Cr_2O_7$
- **c.** nitrogen in 85.0 mg of the amino acid lysine, $C_6H_{14}N_2O_2$
- **d.** cobalt in 2.84 g cobalt(II) acetate, $Co(C_2H_3O_2)_2$

Hydrates

135. Calculate the percentage of water in each of the following hydrates.
- **a.** sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$
- **b.** nickel(II) iodide hexahydrate, $NiI_2 \cdot 6H_2O$
- **c.** ammonium hexacyanoferrate(III) trihydrate (commonly called ammonium ferricyanide), $(NH_4)_2Fe(CN)_6 \cdot 3H_2O$
- **d.** aluminum bromide hexahydrate

Mixed Review

136. Write formulas for the following compounds and determine the percentage composition of each.
- **a.** nitric acid
- **b.** ammonia
- **c.** mercury(II) sulfate
- **d.** antimony(V) fluoride

137. Calculate the percentage composition of the following compounds.
- **a.** lithium bromide, LiBr
- **b.** anthracene, $C_{14}H_{10}$
- **c.** ammonium nitrate, NH_4NO_3
- **d.** nitrous acid, HNO_2
- **e.** silver sulfide, Ag_2S
- **f.** iron(II) thiocyanate, $Fe(SCN)_2$
- **g.** lithium acetate
- **h.** nickel(II) formate

138. Calculate the percentage of the given element in each of the following compounds.
- **a.** nitrogen in urea, NH_2CONH_2
- **b.** sulfur in sulfuryl chloride, SO_2Cl_2
- **c.** thallium in thallium(III) oxide, Tl_2O_3
- **d.** oxygen in potassium chlorate, $KClO_3$
- **e.** bromine in calcium bromide, $CaBr_2$
- **f.** tin in tin(IV) oxide, SnO_2

139. Calculate the mass of the given element in each of the following quantities.
- **a.** oxygen in 4.00 g of manganese dioxide, MnO_2
- **b.** aluminum in 50.0 metric tons of aluminum oxide, Al_2O_3
- **c.** silver in 325 g silver cyanide, AgCN
- **d.** gold in 0.780 g of gold(III) selenide, Au_2Se_3
- **e.** selenium in 683 g sodium selenite, Na_2SeO_3
- **f.** chlorine in 5.0×10^4 g of 1,1-dichloropropane, $CHCl_2CH_2CH_3$

140. Calculate the percentage of water in each of the following hydrates.
- **a.** strontium chloride hexahydrate, $SrCl_2 \cdot 6H_2O$
- **b.** zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$
- **c.** calcium fluorophosphate dihydrate, $CaFPO_3 \cdot 2H_2O$
- **d.** beryllium nitrate trihydrate, $Be(NO_3)_2 \cdot 3H_2O$

141. Calculate the percentage of the given element in each of the following hydrates. You must first determine the formulas of the hydrates.
- **a.** nickel in nickel(II) acetate tetrahydrate
- **b.** chromium in sodium chromate tetrahydrate
- **c.** cerium in cerium(IV) sulfate tetrahydrate

142. Cinnabar is a mineral that is mined in order to produce mercury. Cinnabar is mercury(II) sulfide, HgS. What mass of mercury can be obtained from 50.0 kg of cinnabar?

143. The minerals malachite, $Cu_2(OH)_2CO_3$, and chalcopyrite, $CuFeS_2$, can be mined to obtain copper metal. How much copper could be obtained from 1.00×10^3 kg of each? Which of the two has the greater copper content?

144. Calculate the percentage of the given element in each of the following hydrates.
- **a.** vanadium in vanadium oxysulfate dihydrate, $VOSO_4 \cdot 2H_2O$
- **b.** tin in potassium stannate trihydrate, $K_2SnO_3 \cdot 3H_2O$
- **c.** chlorine in calcium chlorate dihydrate, $CaClO_3 \cdot 2H_2O$

145. Heating copper sulfate pentahydrate will evaporate the water from the crystals, leaving anhydrous copper sulfate, a white powder. *Anhydrous* means "without water." What mass of anhydrous $CuSO_4$ would be produced by heating 500.0 g of $CuSO_4 \cdot 5H_2O$?

146. Silver metal may be precipitated from a solution of silver nitrate by placing a copper strip into the solution. What mass of $AgNO_3$ would you dissolve in water in order to get 1.00 g of silver?

147. A sample of Ag_2S has a mass of 62.4 g. What mass of each element could be obtained by decomposing this sample?

148. A quantity of epsom salts, magnesium sulfate heptahydrate, $MgSO_4 \cdot 7H_2O$, is heated until all the water is driven off. The sample loses 11.8 g in the process. What was the mass of the original sample?

149. The process of manufacturing sulfuric acid begins with the burning of sulfur. What mass of sulfur would have to be burned in order to produce 1.00 kg of H_2SO_4? Assume that all of the sulfur ends up in the sulfuric acid.

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Empirical Formulas, Section 7-4

150. Determine the empirical formula for compounds that have the following analyses.
- **a.** 28.4% copper, 71.6% bromine
- **b.** 39.0% potassium, 12.0% carbon, 1.01% hydrogen, and 47.9% oxygen
- **c.** 77.3% silver, 7.4% phosphorus, 15.3% oxygen
- **d.** 0.57% hydrogen, 72.1% iodine, 27.3% oxygen

151. Determine the simplest formula for compounds that have the following analyses. The data may not be exact.
- **a.** 36.2% aluminum and 63.8% sulfur
- **b.** 93.5% niobium and 6.50% oxygen
- **c.** 57.6% strontium, 13.8% phosphorus, and 28.6% oxygen
- **d.** 28.5% iron, 48.6% oxygen, and 22.9% sulfur

152. Determine the molecular formula of each of the following unknown substances.
- **a.** empirical formula CH_2
  experimental molar mass 28 g/mol
- **b.** empirical formula B_2H_5
  experimental molar mass 54 g/mol
- **c.** empirical formula C_2HCl
  experimental molar mass 179 g/mol
- **d.** empirical formula C_6H_8O
  experimental molar mass 290 g/mol
- **e.** empirical formula C_3H_2O
  experimental molar mass 216 g/mol

Mixed Review

153. Determine the empirical formula for compounds that have the following analyses.
- **a.** 66.0% barium and 34.0% chlorine
- **b.** 80.38% bismuth, 18.46% oxygen, and 1.16% hydrogen
- **c.** 12.67% aluminum, 19.73% nitrogen, and 67.60% oxygen
- **d.** 35.64% zinc, 26.18% carbon, 34.88% oxygen, and 3.30% hydrogen
- **e.** 2.8% hydrogen, 9.8% nitrogen, 20.5% nickel, 44.5% oxygen, and 22.4% sulfur
- **f.** 8.09% carbon, 0.34% hydrogen, 10.78% oxygen, and 80.78% bromine

154. Sometimes, instead of percentage composition, you will have the composition of a sample by mass. Using the actual mass of the sample, determine the empirical formula for compounds that have the following analyses.
- **a.** a 0.858 g sample of an unknown substance is composed of 0.537 g of copper and 0.321 g of fluorine
- **b.** a 13.07 g sample of an unknown substance is composed of 9.48 g of barium, 1.66 g of carbon, and 1.93 g of nitrogen
- **c.** a 0.025 g sample of an unknown substance is composed of 0.0091 g manganese, 0.0106 g oxygen, and 0.0053 g sulfur

155. Determine the empirical formula for compounds that have the following analyses.
- **a.** a 0.0082 g sample contains 0.0015 g of nickel and 0.0067 g of iodine
- **b.** a 0.470 g sample contains 0.144 g of manganese, 0.074 g of nitrogen, and 0.252 g of oxygen
- **c.** a 3.880 g sample contains 0.691 g of magnesium, 1.824 g of sulfur, and 1.365 g of oxygen
- **d.** a 46.25 g sample contains 14.77 g of potassium, 9.06 g of oxygen, and 22.42 g of tin

156. Determine the empirical formula for compounds that have the following analyses:
- **a.** 60.9% As and 39.1% S
- **b.** 76.89% Re and 23.12% O
- **c.** 5.04% H, 35.00% N, and 59.96% O
- **d.** 24.3% Fe, 33.9% Cr, and 41.8% O
- **e.** 54.03% C, 37.81% N, and 8.16% H
- **f.** 55.81% C, 3.90% H, 29.43% F, and 10.85% N

157. Determine the molecular formulas for compounds having the following empirical formulas and molar masses.
- **a.** C_2H_4S; experimental molar mass 179
- **b.** C_2H_4O; experimental molar mass 176
- **c.** $C_2H_3O_2$; experimental molar mass 119
- **d.** C_2H_2O, experimental molar mass 254

158. Use the experimental molar mass to determine the molecular formula for compounds having the following analyses.
- **a.** 41.39% carbon, 3.47% hydrogen, and 55.14% oxygen; experimental molar mass 116.07
- **b.** 54.53% carbon, 9.15% hydrogen, and 36.32% oxygen; experimental molar mass 88
- **c.** 64.27% carbon, 7.19% hydrogen, and 28.54% oxygen; experimental molar mass 168.19

159. A 0.400 g sample of a white powder contains 0.141 g of potassium, 0.115 g of sulfur, and 0.144 g of oxygen. What is the empirical formula for the compound?

160. A 10.64 g sample of a lead compound is analyzed and found to be made up of 9.65 g of lead and 0.99 g of oxygen. Determine the empirical formula for this compound.

161. A 2.65 g sample of a salmon-colored powder contains 0.70 g of chromium, 0.65 g of sulfur, and 1.30 g of oxygen. The molar mass is 392.2. What is the formula of the compound?

162. Ninhydrin is a compound that reacts with amino acids and proteins to produce a dark-colored complex. It is used by forensic chemists and detectives to see fingerprints that might otherwise be invisible. Ninhydrin's composition is 60.68% carbon, 3.40% hydrogen, and 35.92% oxygen. What is the empirical formula for ninhydrin?

163. Histamine is a substance that is released by cells in response to injury, infection, stings, and materials that cause allergic responses, such as pollen. Histamine causes dilation of blood vessels and swelling due to accumulation of fluid in the tissues. People sometimes take *anti*histamine drugs to counteract the effects of histamine. A sample of histamine having a mass of 385 mg is composed of 208 mg of carbon, 31 mg of hydrogen, and 146 mg of nitrogen. The molar mass of histamine is 111 g/mol. What is the molecular formula for histamine?

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164. You analyze two substances in the laboratory and discover that each has the empirical formula CH_2O. You can easily see that they are different substances because one is a liquid with a sharp, biting odor and the other is an odorless, crystalline solid. How can you account for the fact that both have the same empirical formula?

Stoichiometry, Sections 9-1; 9-2

165. How many moles of sodium will react with water to produce 4.0 mol of hydrogen in the following reaction?

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

166. How many moles of lithium chloride will be formed by the reaction of chlorine with 0.046 mol of lithium bromide in the following reaction?

$$2LiBr(aq) + Cl_2(g) \rightarrow 2LiCl(aq) + Br_2(l)$$

167. Aluminum will react with sulfuric acid in the following reaction.

$$2Al(s) + 3H_2SO_4(l) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$$

a. How many moles of H_2SO_4 will react with 18 mol Al?
b. How many moles of each product will be produced?

168. Propane burns in excess oxygen according to the following reaction.

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

a. How many moles each of CO_2 and H_2O are formed from 3.85 mol of propane?
b. If 0.647 mol of oxygen are used in the burning of propane, how many moles each of CO_2 and H_2O are produced? How many moles of C_3H_8 are consumed?

169. Phosphorus burns in air to produce a phosphorus oxide in the following reaction:

$$4P(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$

a. What mass of phosphorus will be needed to produce 3.25 mol of P_4O_{10}?
b. If 0.489 mol of phosphorus burns, what mass of oxygen is used? What mass of P_4O_{10} is produced?

170. Hydrogen peroxide breaks down, releasing oxygen, in the following reaction.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

a. What mass of oxygen is produced when 1.840 mol of H_2O_2 decompose?
b. What mass of water is produced when 5.0 mol O_2 is produced by this reaction?

171. Sodium carbonate reacts with nitric acid according to the following equation:

$$Na_2CO_3(s) + 2HNO_3 \rightarrow 2NaNO_3 + CO_2 + H_2O$$

a. How many moles of Na_2CO_3 are required to produce 100.0 g of $NaNO_3$?
b. If 7.50 g of Na_2CO_3 reacts, how many moles of CO_2 are produced?

172. Hydrogen is generated by passing hot steam over iron, which oxidizes to form Fe_3O_4, in the following equation:

$$3Fe(s) + 4H_2O(g) \rightarrow 4H_2(g) + Fe_3O_4(s)$$

a. If 625 g of Fe_3O_4 is produced in the reaction, how many moles of hydrogen are produced at the same time?
b. How many moles of iron would be needed to generate 27 g of hydrogen?

173. Calculate the mass of silver bromide produced from 22.5 g of silver nitrate in the following reaction:

$$2AgNO_3(aq) + MgBr_2(aq) \rightarrow 2AgBr(s) + Mg(NO_3)_2(aq)$$

174. What mass of acetylene, C_2H_2, will be produced from the reaction of 90. g of calcium carbide, CaC_2, with water in the following reaction?

$$CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$$

175. Chlorine gas can be produced in the laboratory by adding concentrated hydrochloric acid to manganese(IV) oxide in the following reaction:

$$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$$

a. Calculate the mass of MnO_2 needed to produce 25.0 g of Cl_2.
b. What mass of $MnCl_2$ is produced when 0.091 g of Cl_2 is generated?

Mixed Review

176. How many moles of ammonium sulfate can be made from the reaction of 30.0 mol of NH_3 with H_2SO_4 according to the following equation:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

177. In a very violent reaction called a thermite reaction, aluminum metal reacts with iron(III) oxide to form iron metal and aluminum oxide according to the following equation:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

a. What mass of Al will react with 150 g of Fe_2O_3?
b. If 0.905 mol Al_2O_3 is produced in the reaction, what mass of Fe is produced?
c. How many moles of Fe_2O_3 will react with 99.0 g of Al?

178. The reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is used to produce ammonia commercially. If 1.40 g of N_2 are used in the reaction, how many grams of H_2 will be needed?

179. What mass of sulfuric acid, H_2SO_4, is required to react with 1.27 g of potassium hydroxide, KOH? The products of this reaction are potassium sulfate and water.

180. Ammonium hydrogen phosphate, $(NH_4)_2HPO_4$, a common fertilizer; is made from reacting phosphoric acid, H_3PO_4, with ammonia.
a. Write the equation for this reaction.
b. If 10.00 g of ammonia react, how many moles of fertilizer will be produced?

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c. What mass of ammonia will react with 2800 kg of H_3PO_4?

181. The following reaction shows the synthesis of zinc citrate, a ingredient in toothpaste, from zinc carbonate and citric acid:

$$3ZnCO_3(s) + 2C_6H_8O_7(aq) \rightarrow Zn_3(C_6H_5O_7)_2(aq) + 3H_2O(l) + 3CO_2(g)$$

a. How many moles of $ZnCO_3$ and $C_6H_8O_7$ are required to produce 30.0 mol of $Zn_3(C_6H_5O_7)_2$?
b. What quantities, in kilograms, of H_2O and CO_2 are produced by the reaction of 500. mol of citric acid?

182. Methyl butanoate, an oily substance with a strong fruity fragrance can be made by reacting butanoic acid with methanol according to the following equation:

$$C_3H_7COOH + CH_3OH \rightarrow C_3H_7COOCH_3 + H_2O$$

a. What mass of methyl butanoate is produced from the reaction of 52.5 g of butanoic acid?
b. In order to purify methyl butanoate, water must be removed. What mass of water is produced from the reaction of 5800. g of methanol?

183. Ammonium nitrate decomposes to yield nitrogen gas, water, and oxygen gas in the following reaction:

$$2NH_4NO_3 \rightarrow 2N_2 + O_2 + 4H_2O$$

a. How many moles of nitrogen gas are produced when 36.0 g of NH_4NO_3 reacts?
b. If 7.35 mol of H_2O are produced in this reaction, what mass of NH_4NO_3 reacted?

184. Lead(II) nitrate reacts with potassium iodide to produce lead(II) iodide and potassium nitrate. If 1.23 mg of lead nitrate are consumed, what is the mass of the potassium nitrate produced?

185. A car battery produces electrical energy with the following chemical reaction:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

If the battery loses 0.34 kg of lead in this reaction, how many moles of lead(II) sulfate are produced?

186. In a space shuttle, the CO_2 that the crew exhales is removed from the air by a reaction within canisters of lithium hydroxide. On average, each astronaut exhales about 20.0 mol of CO_2 daily. What mass of water will be produced when this amount reacts with LiOH? The other product of the reaction is Li_2CO_3.

187. Water is sometimes removed from the products of a reaction by placing them in a closed container with excess P_4O_{10}. Water is absorbed by the following reaction:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

a. What mass of water can be absorbed by 1.00×10^2 g of P_4O_{10}?
b. If the P_4O_{10} in the container absorbs 0.614 mol of water, what mass of H_3PO_4 is produced?
c. If the mass of the container of P_4O_{10} increases from 56.64 g to 63.70 g, how many moles of water are absorbed?

188. Ethanol, C_2H_5OH, is considered a clean fuel because it burns in oxygen to produce carbon dioxide and water with few trace pollutants. If 95.0 g of H_2O are produced during the combustion of ethanol, how many grams of ethanol were present at the beginning of the reaction?

189. Sulfur dioxide is one of the major contributors to acid rain. Sulfur dioxide can react with oxygen and water in the atmosphere to form sulfuric acid, as shown in the following equation:

$$2H_2O(l) + O_2(g) + 2SO_2(g) \rightarrow 2H_2SO_4(aq)$$

If 50.0 g of sulfur dioxide from pollutants reacts with water and oxygen found in the air, how many grams of sulfuric acid can be produced? How many grams of oxygen are used in the process?

190. When heated, sodium bicarbonate, $NaHCO_3$, decomposes into sodium carbonate, Na_2CO_3, water, and carbon dioxide. If 5.00 g of $NaHCO_3$ decomposes, what is the mass of the carbon dioxide produced?

191. A reaction between hydrazine, N_2H_4, and dinitrogen tetroxide, N_2O_4, has been used to launch rockets into space. The reaction produces nitrogen gas and water vapor.
a. Write a balanced chemical equation for this reaction.
b. What is the mole ratio of N_2O_4 to N_2?
c. How many moles of N_2 will be produced if 20 000 mol of N_2H_4 are used by a rocket?
d. How many grams of H_2O are made when 450. kg of N_2O_4 are consumed?

192. Joseph Priestley is credited with the discovery of oxygen. He produced O_2 by heating mercury(II) oxide, HgO, to decompose it into its elements. How many moles of oxygen could Priestley have produced if he had decomposed 517.84 g of mercury oxide?

193. Iron(III) chloride, $FeCl_3$, can be made by the reaction of iron with chlorine gas. How much iron, in grams, will be needed to completely react with 58.0 g of Cl_2?

194. Sodium sulfide and cadmium nitrate undergo a double-replacement reaction as shown by the following equation:

$$Na_2S + Cd(NO_3)_2 \rightarrow 2NaNO_3 + CdS$$

What is the mass, in milligrams, of cadmium sulfide that can be made from 5.00 mg of sodium sulfide?

195. Potassium permanganate and glycerin react explosively according to the following equation:

$$14KMnO_4 + 4C_3H_5(OH)_3 \rightarrow 7K_2CO_3 + 7Mn_2O_3 + 5CO_2 + 16H_2O$$

a. How many moles of carbon dioxide can be produced from 4.44 mol of $KMnO_4$?
b. If 5.21 g of H_2O are produced, how many moles of glycerin, $C_3H_5(OH)_3$, were used?
c. If 3.39 mol of potassium carbonate are made, how many grams of manganese(III) oxide are also made?
d. How many grams of glycerin will be needed to react with 50.0 g of $KMnO_4$? How many grams of CO_2 will be produced in the same reaction?

196. Calcium carbonate found in limestone and marble reacts with hydrochloric acid to form calcium chloride,

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carbon dioxide, and water according to the following equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

a. What mass of HCl will be needed to produce 5.00×10^3 kg of $CaCl_2$?
b. What mass of CO_2 could be produced from the reaction of 750 g of $CaCO_3$?

197. The fuel used to power the booster rockets on the space shuttle is a mixture of aluminum metal and ammonium perchlorate. The following balanced equation represents the reaction of these two ingredients:

$$3Al(s) + 3NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(g) + 3NO(g) + 6H_2O(g)$$

a. If 1.50×10^5 g of Al react, what mass of NH_4ClO_4, in grams, is required?
b. If aluminum reacts with 620 kg of NH_4ClO_4, what mass of nitrogen monoxide is produced?

198. Phosphoric acid is typically produced by the action of sulfuric acid on rock that has a high content of calcium phosphate according to the following equation:

$$3H_2SO_4 + Ca_3(PO_4)_2 + 6H_2O \rightarrow 3[CaSO_4 \cdot 2H_2O] + 2H_3PO_4$$

a. If 2.50×10^5 kg of H_2SO_4 react, how many moles of H_3PO_4 can be made?
b. What mass of calcium sulfate dihydrate is produced by the reaction of 400. kg of calcium phosphate?
c. If the rock being used contains 78.8% $Ca_3(PO_4)_2$, how many metric tons of H_3PO_4 can be produced from 68 metric tons of rock?

199. Rusting of iron occurs in the presence of moisture according to the following equation:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Suppose that 3.19% of a heap of steel scrap with a mass of 1650 kg rusts in a year. What mass will the heap have after one year of rusting?

Limiting Reactants, Section 9-3

200. Aluminum oxidizes according to the following equation:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

Powdered Al (0.048 mol) is placed into a container containing 0.030 mol O_2. What is the limiting reactant?

201. A process by which zirconium metal can be produced from the mineral zirconium(IV) orthosilicate, $ZrSiO_4$, starts by reacting it with chlorine gas to form zirconium(IV) chloride:

$$ZrSiO_4 + 2Cl_2 \rightarrow ZrCl_4 + SiO_2 + O_2$$

What mass of $ZrCl_4$ can be produced if 862 g of $ZrSiO_4$ and 950. g of Cl_2 are available? You must first determine the limiting reactant.

Mixed Review

202. Heating zinc sulfide in the presence of oxygen yields the following:

$$ZnS + O_2 \rightarrow ZnO + SO_2$$

If 1.72 mol of ZnS is heated in the presence of 3.04 mol of O_2, which reactant will be used up? Balance the equation first.

203. Use the following equation for the oxidation of aluminum in the following problems:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

a. Which reactant is limiting if 0.32 mol Al and 0.26 mol O_2 are available?
b. How many moles of Al_2O_3 are formed from the reaction of 6.38×10^{-3} mol of O_2 and 9.15×10^{-3} mol of Al?
c. If 3.17 g of Al and 2.55 g of O_2 are available, which reactant is limiting?

204. In the production of copper from ore containing copper(II) sulfide, the ore is first roasted to change it to the oxide according to the following equation:

$$2CuS + 3O_2 \rightarrow 2CuO + 2SO_2$$

a. If 100 g of CuS and 56 g of O_2 are available, which reactant is limiting?
b. What mass of CuO can be formed from the reaction of 18.7 g of CuS and 12.0 g of O_2?

205. A reaction such as the one shown here is often used to demonstrate a single replacement reaction:

$$3CuSO_4(aq) + 2Fe(s) \rightarrow 3Cu(s) + Fe_2(SO_4)_3(aq)$$

If you place 0.092 mol of iron filings in a solution containing 0.158 mol of $CuSO_4$, what is the limiting reactant? How many moles of Cu will be formed?

206. In the reaction $BaCO_3 + 2HNO_3 \rightarrow Ba(NO_3)_2 + CO_2 + H_2O$, what mass of $Ba(NO_3)_2$ can be formed by combining 55 g $BaCO_3$ and 26 g HNO_3?

207. Bromine replaces iodine in magnesium iodide by the following process:

$$MgI_2 + Br_2 \rightarrow MgBr_2 + I_2$$

a. Which is the excess reactant when 560 g of MgI_2 and 360 g of Br_2 react, and what mass remains?
b. What mass of I_2 is formed in the same process?

208. Nickel replaces silver from silver nitrate in solution according to the following equation:

$$2AgNO_3 + Ni \rightarrow 2Ag + Ni(NO_3)_2$$

a. If you have 22.9 g of Ni and 112 g of $AgNO_3$, which reactant is in excess?
b. What mass of nickel(II) nitrate would be produced given the quantities above?

209. Carbon disulfide, CS_2, is an important industrial substance. Its fumes can burn explosively in air to form sulfur dioxide and carbon dioxide:

$$CS_2(g) + O_2(g) \rightarrow SO_2(g) + CO_2(g)$$

If 1.60 mol of CS_2 burns with 5.60 mol of O_2, how many moles of the excess reactant will still be present when the reaction is over?

210. Although poisonous, mercury compounds were once used to kill bacteria in wounds and on the skin. One was called "ammoniated mercury" and is made from mercury(II) chloride according to the following equation:

$$HgCl_2(aq) + 2NH_3(aq) \rightarrow Hg(NH_2)Cl(s) + NH_4Cl(aq)$$

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a. What mass of $Hg(NH_2)Cl$ could be produced from 0.91 g of $HgCl_2$ assuming plenty of ammonia is available?
b. What mass of $Hg(NH_2)Cl$ could be produced from 0.91 g of $HgCl_2$ and 0.15 g of NH_3 in solution?

211. Aluminum chips are sometimes added to sodium hydroxide-based drain cleaners because they react to generate hydrogen gas which bubbles and helps loosen material in the drain. The equation follows:

$$Al(s) + NaOH(aq) + H_2O(l) \rightarrow NaAlO_2(aq) + H_2(g)$$

a. Balance the equation.
b. How many moles of H_2 can be generated from 0.57 mol Al and 0.37 mol NaOH in excess water?
c. Which reactant should be limiting in order for the mixture to be most effective as a drain cleaner? Explain your choice.

212. Copper is changed to copper(II) ions by nitric acid according to the following equation:

$$4HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

a. How many moles each of HNO_3 and Cu must react in order to produce 0.0845 mol of NO_2?
b. If 5.94 g of Cu and 23.23 g of HNO_3 are combined, which reactant is in excess?

213. One industrial process for producing nitric acid begins with the following reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

a. If 2.90 mol NH_3 and 3.75 mol O_2 are available, how many moles of each product are formed?
b. Which reactant is limiting if 4.20×10^4 g of NH_3 and 1.31×10^5 g of O_2 are available?
c. What mass of NO is formed in the reaction of 869 kg of NH_3 and 2480 kg O_2?

214. Acetaldehyde, CH_3CHO, is manufactured by the reaction of ethanol with copper(II) oxide according to the following equation:

$$CH_3CH_2OH + CuO \rightarrow CH_3CHO + H_2O + Cu$$

What mass of acetaldehyde can be produced by the reaction between 620 g of ethanol and 1020 g of CuO? What mass of which reactant will be left over?

215. Hydrogen bromide can be produced by a reaction among bromine, sulfur dioxide, and water as follows:

$$SO_2 + Br_2 + H_2O \rightarrow 2HBr + H_2SO_4$$

If 250 g of SO_2 and 650 g of Br_2 react in the presence of excess water, what mass of HBr will be formed?

216. Sulfur dioxide can be produced in the laboratory by the reaction of hydrochloric acid and a sulfite salt such as sodium sulfite:

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O$$

What mass of SO_2 can be made from 25.0 g of Na_2SO_3 and 22.0 g of HCl?

217. The rare-earth metal terbium is produced from terbium(III) fluoride and calcium metal by the following single replacement reaction:

$$2TbF_3 + 3Ca \rightarrow 3CaF_2 + 2Tb$$

a. Given 27.5 g of TbF_3 and 6.96 g of Ca, how many grams of terbium could be produced?
b. How many grams of the excess reactant is left over?

Percent Yield, Section 9-3

218. Calculate the percent yield in each of the following cases.
a. theoretical yield is 50.0 g of product; actual yield is 41.9 g
b. theoretical yield is 290 kg of product; actual yield is 270 kg
c. theoretical yield is 6.05×10^4 kg of product; actual yield is 4.18×10^4 kg
d. theoretical yield is 0.00192 g of product; actual yield is 0.00089 g

219. In the commercial production of the element arsenic, arsenic(III) oxide is heated with carbon, which reduces the oxide to the metal according to the following equation:

$$2As_2O_3 + 3C \rightarrow 3CO_2 + 4As$$

a. If 8.87 g of As_2O_3 is used in the reaction and 5.33 g of As is produced, what is the percent yield?
b. If 67 g of carbon is used up in a different reaction and 425 g of As is produced, calculate the percent yield of this reaction.

Mixed Review

220. Ethyl acetate is a sweet-smelling solvent used in varnishes and fingernail-polish remover. It is produced industrially by heating acetic acid and ethanol together in the presence of sulfuric acid, which is added to speed up the reaction. The ethyl acetate is distilled off as it is formed. The equation for the process is as follows:

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow{H_2SO_4} \underset{\text{ethyl acetate}}{CH_3COOCH_2CH_3} + H_2O$$

Determine the percent yield in the following cases.
a. 68.3 g of ethyl acetate should be produced but only 43.9 g is recovered.
b. 0.0419 mol of ethyl acetate is produced but 0.0722 mol is expected. (Hint: Percent yield can also be calculated by dividing the actual yield in moles by the theoretical yield in moles.)
c. 4.29 mol of ethanol is reacted with excess acetic acid, but only 2.98 mol of ethyl acetate is produced.
d. A mixture of 0.58 mol ethanol and 0.82 mol acetic acid is reacted and 0.46 mol ethyl acetate is produced. (Hint: What is the limiting reactant?)

221. Assume the following hypothetical reaction takes place:

$$2A + 7B \rightarrow 4C + 3D$$

Calculate the percent yield in each of the following cases.
a. The reaction of 0.0251 mol of A produces 0.0349 mol of C.

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b. The reaction of 1.19 mol of A produces 1.41 mol of D.
c. The reaction of 189 mol of B produces 39 mol of D.
d. The reaction of 3500 mol of B produces 1700 mol of C.

222. Elemental phosphorus can be produced by heating calcium phosphate from rocks with silica sand (SiO_2) and carbon in the form of coke. The following reaction takes place:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 2P + 5CO$$

a. If 57 mol of $Ca_3(PO_4)_2$ is used and 101 mol of $CaSiO_3$ is obtained, what is the percent yield?
b. Determine the percent yield obtained if 1280 mol of carbon is consumed and 622 mol of $CaSiO_3$ is produced.
c. The engineer in charge of this process expects a yield of 81.5%. If 1.4×10^5 mol of $Ca_3(PO_4)_2$ is used, how many moles of phosphorus will be produced?

223. Tungsten (W) can be produced from its oxide by reacting the oxide with hydrogen at a high temperature according to the following equation:

$$WO_3 + 3H_2 \rightarrow W + 3H_2O$$

a. What is the percent yield if 56.9 g of WO_3 yields 41.4 g of tungsten?
b. How many moles of tungsten will be produced from 3.72 g of WO_3 if the yield is 92.0%?
c. A chemist carries out this reaction and obtains 11.4 g of tungsten. If the percent yield is 89.4%, what mass of WO_3 was used?

224. Carbon tetrachloride, CCl_4, is a solvent that was once used in large quantities in dry cleaning. Because it is a dense liquid that does not burn, it was also used in fire extinguishers. Unfortunately, its use was discontinued because it was found to be a carcinogen. It was manufactured by the following reaction:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

The reaction was economical because the byproduct disulfur dichloride, S_2Cl_2, could be used by industry in the manufacture of rubber products and other materials.
a. What is the percent yield of CCl_4 if 719 kg is produced from the reaction of 410. kg of CS_2?
b. If 67.5 g of Cl_2 are used in the reaction and 39.5 g of S_2Cl_2 is produced, what is the percent yield?
c. If the percent yield of the industrial process is 83.3%, how many kilograms of CS_2 should be reacted to obtain 5.00×10^4 kg of CCl_4? How many kilograms of S_2Cl_2 will be produced, assuming the same yield for that product?

225. Nitrogen dioxide, NO_2, can be converted to dinitrogen pentoxide, N_2O_5, by reacting it with ozone, O_3. The reaction of NO_2 takes place according to the following equation:

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(s \text{ or } g) + O_2(g)$$

a. Calculate the percent yield for a reaction in which 0.38 g of NO_2 reacts and 0.36 g of N_2O_5 is recovered.
b. What mass of N_2O_5 will result from the reaction of 6.0 mol of NO_2 if there is a 61.1% yield in the reaction?

226. In the past, hydrogen chloride, HCl, was made using the *salt-cake* method as shown in the following equation:

$$2NaCl(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(s) + 2HCl(g)$$

If 30.0 g of NaCl and 0.250 mol of H_2SO_4 are available, and 14.6 g of HCl is made, what is the percent yield?

227. Cyanide compounds such as sodium cyanide, NaCN, are especially useful in gold refining because they will react with gold to form a stable compound that can then be separated and broken down to retrieve the gold. Ore containing only small quantities of gold can be used in this form of "chemical mining." The equation for the reaction follows:

$$4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4NaAu(CN)_2 + 4NaOH$$

a. What percent yield is obtained if 410 g of gold produces 540 g of $NaAu(CN)_2$?
b. Assuming a 79.6% yield in the conversion of gold to $NaAu(CN)_2$, what mass of gold would produce 1.00 kg of $NaAu(CN)_2$?
c. Given the conditions in (b), what mass of gold ore that is 0.001% gold would be needed to produce 1.00 kg of $NaAu(CN)_2$?

228. Diiodine pentoxide is useful in devices such as respirators because it reacts with the dangerous gas carbon monoxide, CO, to produce relatively harmless CO_2 according to the following equation:

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

a. In testing a respirator, 2.00 g of carbon monoxide gas is passed through diiodine pentoxide. Upon analyzing the results, it is found that 3.17 g of I_2 was produced. Calculate the percent yield of the reaction.
b. Assuming that the yield in (a) resulted because some of the CO did not react, calculate the mass of CO that passed through.

229. Sodium hypochlorite, NaClO, the main ingredient in household bleach, is produced by bubbling chlorine gas through a strong lye (sodium hydroxide, NaOH) solution. The following equation shows the reaction that occurs:

$$2NaOH(aq) + Cl_2(g) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$$

a. What is the percent yield of the reaction if 1.2 kg of Cl_2 reacts to form 0.90 kg of NaClO?
b. If a plant operator wants to make 25 metric tons of NaClO per day at a yield of 91.8%, how many metric tons of chlorine gas must be on hand each day?
c. What mass of NaCl is formed per mole of chlorine gas at a yield of 81.8%?
d. At what rate in kg per hour must NaOH be replenished if the reaction produces 370 kg/h of NaClO at a yield of 79.5%? Assume that all of the NaOH reacts to produce this yield.

230. Magnesium burns in oxygen to form magnesium oxide. However, when magnesium burns in air, which is only about one-fifth oxygen, side reactions form other products, such as magnesium nitride, Mg_3N_2.

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a. Write a balanced equation for the burning of magnesium in oxygen.
b. If enough magnesium burns in air to produce 2.04 g of magnesium oxide but only 1.79 g is obtained, what is the percent yield?
c. Magnesium will react with pure nitrogen to form the nitride, Mg_3N_2. Write a balanced equation for this reaction.
d. If 0.097 mol of Mg react with nitrogen and 0.027 mol of Mg_3N_2 is produced, what is the percent yield of the reaction?

231. Some alcohols can be converted to organic acids by using sodium dichromate and sulfuric acid. The following equation shows the reaction of 1-propanol to propanoic acid:

$$3CH_3CH_2CH_2OH + 2Na_2Cr_2O_7 + 8H_2SO_4 \rightarrow 3CH_3CH_2COOH + 2Cr_2(SO_4)_3 + 2Na_2SO_4 + 11H_2O$$

a. If 0.89 g of 1-propanol reacts and 0.88 g of propanoic acid is produced, what is the percent yield?
b. A chemist uses this reaction to obtain 1.50 mol of propanoic acid. The reaction consumes 136 g of propanol. Calculate the percent yield.
c. Some 1-propanol of uncertain purity is used in the reaction. If 116 g of $Na_2Cr_2O_7$ are consumed in the reaction and 28.1 g of propanoic acid are produced, what is the percent yield?

232. Acrylonitrile, $C_3H_3N(g)$, is an important ingredient in the production of various fibers and plastics. Acrylonitrile is produced from the following reaction:

$$C_3H_6(g) + NH_3(g) + O_2(g) \rightarrow C_3H_3N(g) + H_2O(g)$$

If 850. g of C_3H_6 is mixed with 300. g of NH_3 and unlimited O_2, to produce 850. g of acrylonitrile, what is the percent yield? You must first balance the equation.

233. Methanol, CH_3OH, is frequently used in race cars as fuel. It is produced as the sole product of the combination of carbon monoxide gas and hydrogen gas.
a. If 430. kg of hydrogen react, what mass of methanol could be produced?
b. If 3.12×10^3 kg of methanol are actually produced, what is the percent yield?

234. The compound, $C_6H_{16}N_2$, is one of the starting materials in the production of nylon. It can be prepared from the following reaction involving adipic acid, $C_6H_{10}O_4$:

$$C_6H_{10}O_4(l) + 2NH_3(g) + 4H_2(g) \rightarrow C_6H_{16}N_2(l) + 4H_2O$$

What is the percent yield if 750. g of adipic acid results in the production of 578 g of $C_6H_{16}N_2$?

235. Plants convert carbon dioxide to oxygen during photosynthesis according to the following equation:

$$CO_2 + H_2O \rightarrow C_6H_{12}O_6 + O_2$$

Balance this equation, and calculate how much oxygen would be produced if 1.37×10^4 g of carbon dioxide reacts with a percent yield of 63.4%.

236. Lime, CaO, is frequently added to streams and lakes which have been polluted by acid rain. The calcium oxide reacts with the water to form a base that can neutralize the acid as shown in the following reaction:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

If 2.67×10^2 mol of base are needed to neutralize the acid in a lake, and the above reaction has a percent yield of 54.3%, what is the mass, in kilograms, of lime that must be added to the lake?

Gas Laws, Section 10-3

Boyle's Law

In each of the following problems, assume that the temperature and molar quantity of gas do not change.

237. Calculate the unknown quantity in each of the following measurements of gases.

	P_1	V_1	P_2	V_2
a.	3.0 atm	25 mL	6.0 atm	? mL
b.	99.97 kPa	550. mL	? kPa	275 mL
c.	0.89 atm	? L	3.56 atm	20.0 L
d.	? kPa	800. mL	500. kPa	160. mL
e.	0.040 atm	? L	250 atm	1.0×10^{-2} L

238. A sample of neon gas occupies a volume of 2.8 L at 1.8 atm. What will its volume be at 1.2 atm?

239. To what pressure would you have to compress 48.0 L of oxygen gas at 99.3 kPa in order to reduce its volume to 16.0 L?

240. A chemist collects 59.0 mL of sulfur dioxide gas on a day when the atmospheric pressure is 0.989 atm. On the next day, the pressure has changed to 0.967 atm. What will the volume of the SO_2 gas be on the second day?

241. 2.2 L of hydrogen at 6.5 atm pressure is used to fill a balloon at a final pressure of 1.15 atm. What is its final volume?

Charles's Law

In each of the following problems, assume that the pressure and molar quantity of gas do not change.

242. Calculate the unknown quantity in each of the following measurements of gases:

	V_1	T_1	V_2	T_2
a.	40.0 mL	280. K	? mL	350. K
b.	0.606 L	300. K	0.404 L	? K
c.	? mL	292 K	250. mL	365 K
d.	100. mL	? K	125 mL	305 K
e.	0.0024 L	22°C	? L	−14°C

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243. A balloon full of air has a volume of 2.75 L at a temperature of 18°C. What is the balloon's volume at 45°C?

244. A sample of argon has a volume of 0.43 mL at 24°C. At what temperature in degrees Celsius will it have a volume of 0.57 mL?

Gay-Lussac's Law

In each of the following problems, assume that the volume and molar quantity of gas do not change.

245. Calculate the unknown quantity in each of the following measurements of gases.

P_1	T_1	P_2	T_2
a. 1.50 atm	273 K	? atm	410 K
b. 0.208 atm	300. K	0.156 atm	? K
c. ? kPa	52°C	99.7 kPa	77°C
d. 5.20 atm	?°C	4.16 atm	−13°C
e. 8.33×10^{-4} atm	−84°C	3.92×10^{-3} atm	? °C

246. A cylinder of compressed gas has a pressure of 4.882 atm on one day. The next day, the same cylinder of gas has a pressure of 4.690 atm, and its temperature is 8°C. What was the temperature on the previous day in °C?

247. A mylar balloon is filled with helium gas to a pressure of 107 kPa when the temperature is 22°C. If the temperature changes to 45°C, what will be the pressure of the helium in the balloon?

The Combined Gas Law

In each of the following problems, it is assumed that the molar quantity of gas does not change.

248. Calculate the unknown quantity in each of the following measurements of gases.

P_1	V_1	T_1	P_2	V_2	T_2
a. 99.3 kPa	225 mL	15°C	102.8 kPa	? mL	24°C
b. 0.959 atm	3.50 L	45°C	? atm	3.70 L	37°C
c. 0.0036 atm	62 mL	373 K	0.0029 atm	64 mL	? K
d. 100. kPa	43.2 mL	19°C	101.3 kPa	? mL	0°C

249. A student collects 450. mL of HCl(g) hydrogen chloride gas at a pressure of 100. kPa and a temperature of 17°C. What is the volume of the HCl at 0°C and 101.3 kPa?

Dalton's Law of Partial Pressures

250. A chemist collects a sample of $H_2S(g)$ over water at a temperature of 27°C. The total pressure of the gas that has displaced a volume of 15 mL of water is 207.33 kPa. What is the pressure of the H_2S gas collected?

In each of the following problems, assume that the molar quantity of gas does not change.

251. Some hydrogen is collected over water at 10°C and 105.5 kPa pressure. The total volume of the sample was 1.93 L. Calculate the volume of the hydrogen corrected to STP.

252. One student carries out a reaction that gives off methane gas and obtains a total volume by water displacement of 338 mL at a temperature of 19°C and a pressure of 0.9566 atm. Another student does the identical experiment on another day at a temperature of 26°C and a pressure of 0.989 atm. Which student collected more CH_4?

Mixed Review

In each of the following problems, assume that the molar quantity of gas does not change.

253. Calculate the unknown quantity in each of the following measurements of gases.

P_1	V_1	P_2	V_2
a. 127.3 kPa	796 cm^3	? kPa	965 cm^3
b. 7.1×10^2 atm	? mL	9.6×10^{-1} atm	3.7×10^3 mL
c. ? kPa	1.77 L	30.79 kPa	2.44 L
d. 114 kPa	2.93 dm^3	4.93×10^4 kPa	? dm^3
e. 1.00 atm	120. mL	? atm	97.0 mL
f. 0.77 atm	3.6 m^3	1.90 atm	? m^3

254. A gas cylinder contains 0.722 m^3 of hydrogen gas at a pressure of 10.6 atm. If the gas is used to fill a balloon at a pressure of 0.96 atm, what is the volume in m^3 of the filled balloon?

255. A weather balloon has a maximum volume of 7.50×10^3 L. The balloon contains 195 L of helium gas at a pressure of 0.993 atm. What will be the pressure when the balloon is at maximum volume?

256. A rubber ball contains 5.70×10^{-1} dm^3 of gas at a pressure of 1.05 atm. What volume will the gas occupy at 7.47 atm?

257. Calculate the unknown quantity in each of the following measurements of gases.

V_1	T_1	V_2	T_2
a. 26.5 mL	? K	32.9 mL	290. K
b. ? dm^3	100.°C	0.83 dm^3	29°C
c. 7.44×10^4 mm^3	870.°C	2.59×10^2 mm^3	? °C
d. 5.63×10^{-2} L	132 K	? L	190. K
e. ? cm^3	243 K	819 cm^3	409 K
f. 679 m^3	−3°C	? m^3	−246°C

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258. A bubble of carbon dioxide gas in some unbaked bread dough has a volume of 1.15 cm^3 at a temperature of 22°C. What volume will the bubble have when the bread is baked and the bubble reaches a temperature of 99°C?

259. A perfectly elastic balloon contains 6.75 dm^3 of air at a temperature of 40.°C. What is the temperature if the balloon has a volume of 5.03 dm^3?

260. Calculate the unknown quantity in each of the following measurements of gases.

	P_1	T_1	P_2	T_2
a.	0.777 atm	?°C	5.6 atm	192°C
b.	152 kPa	302 K	? kPa	11 K
c.	? atm	−76°C	3.97 atm	27°C
d.	395 atm	46°C	706 atm	?°C
e.	? atm	−37°C	350. atm	2050°C
f.	0.39 atm	263 K	0.058 atm	? K

261. A 2 L bottle containing only air is sealed at a temperature of 22°C and a pressure of 0.982 atm. The bottle is placed in a freezer and allowed to cool to −3°C. What is the pressure in the bottle?

262. The pressure in a car tire is 2.50 atm at a temperature of 33°C . What would the pressure be if the tire were allowed to cool to 0°C? Assume that the tire does not change volume.

263. A container filled with helium gas has a pressure of 127.5 kPa at a temperature of 290. K. What is the temperature when the pressure is 3.51 kPa?

264. Calculate the unknown quantity in each of the following measurements of gases.

	P_1	V_1	T_1	P_2	V_2	T_2
a.	1.03 atm	1.65 L	19°C	0.920 atm	? L	46°C
b.	107.0 kPa	3.79 dm^3	73°C	? kPa	7.58 dm^3	217°C
c.	0.029 atm	249 mL	? K	0.098 atm	197 mL	293 K
d.	113 kPa	? mm^3	12°C	149 kPa	3.18×10^3 mm^3	−18°C
e.	1.15 atm	0.93 m^3	−22°C	1.01 atm	0.85 m^3	?°C
f.	? atm	156 cm^3	195 K	2.25 atm	468 cm^3	585 K

265. A scientist has a sample of gas that was collected several days earlier. The sample has a volume of 392 cm^3 at a pressure of 0.987 atm and a temperature of 21°C. On the day the gas was collected, the temperature was 13°C and the pressure was 0.992 atm. What volume did the gas have on the day it was collected?

266. Hydrogen gas is collected by water displacement. Total volume collected is 0.461 L at a temperature of 17°C and a pressure of 0.989 atm. What is the pressure of dry hydrogen gas collected?

267. One container with a volume of 1.00 L contains argon at a pressure of 1.77 atm, and a second container of 1.50 L volume contains argon at a pressure of 0.487 atm. They are then connected to each other so that the pressure can become equal in both containers. What is the equalized pressure? Hint: Each sample of gas now occupies the total space. Dalton's law of partial pressures applies here.

268. Oxygen gas is collected over water at a temperature of 10.°C and a pressure of 1.02 atm. The volume of gas plus water vapor collected is 293 mL. What volume of oxygen at STP was collected?

269. A 500 mL bottle is partially filled with water so that the total volume of gases (water vapor and air) remaining in the bottle is 325 cm^3, measured at 20.°C and 101.3 kPa. The bottle is sealed and taken to a mountaintop where the pressure is 76.24 kPa and the temperature is 10°C. If the bottle is upside down and the seal leaks, how much water will leak out? The key to this problem is to determine the pressure in the 325 cm^3 space when the bottle is at the top of the mountain.

270. An air thermometer can be constructed by using a glass bubble attached to a piece of small-diameter glass tubing. The tubing contains a small amount of colored water that rises when the temperature increases and the trapped air expands. You want a 0.20 cm^3 change in volume to equal a 1°C change in temperature. What total volume of air at 20.°C should be trapped in the apparatus below the liquid?

271. A sample of nitrogen gas is collected over water, yielding a total volume of 62.25 mL at a temperature of 22°C and a total pressure of 97.7 kPa. At what pressure will the nitrogen alone occupy a volume of 50.00 mL at the same temperature?

272. The theoretical yield of a reaction that gives off nitrogen trifluoride gas is 844 mL at STP. What total volume of NF_3 plus water vapor will be collected over water at 25°C and a total pressure of 1.017 atm?

273. A weather balloon is inflated with 2.94 kL of helium at a location where the pressure is 1.06 atm and the temperature is 32°C. What will be the volume of the balloon at an altitude where the pressure is 0.092 atm and the temperature is −35°C?

274. The safety limit for a certain can of aerosol spray is 95°C. If the pressure of the gas in the can is 2.96 atm when it is 17°C, what will the pressure be at the safety limit?

275. A chemistry student collects a sample of ammonia gas at a temperature of 39°C. Later, the student measures the volume of the ammonia as 108 mL, but its temperature is now 21°C. What was the volume of the ammonia when it was collected?

276. A quantity of CO_2 gas occupies a volume of 624 L at a pressure of 1.40 atm. If this CO_2 is pumped into a gas

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cylinder that has a volume of 80.0 L, what pressure will the CO_2 exert on the cylinder?

The Ideal Gas Law, Section 11-2

277. Use the ideal-gas-law equation to calculate the unknown quantity in each of the following sets of measurements. You will need to convert Celsius temperatures to Kelvin temperatures and volume units to liters.

P	*V*	*n*	*T*
a. 1.09 atm	? L	0.0881 mol	302 K
b. 94.9 kPa	0.0350 L	? mol	55°C
c. ? kPa	15.7 L	0.815 mol	−20.°C
d. 0.500 atm	629 mL	0.0337 mol	? K
e. 0.950 atm	? L	0.0818 mol	19°C
f. 107 kPa	39.0 mL	? mol	27°C

278. A student collects 425 mL of oxygen at a temperature of 24°C and a pressure of 0.899 atm. How many moles of oxygen did the student collect?

Applications of the Ideal Gas Law

279. A sample of an unknown gas has a mass of 0.116 g. It occupies a volume of 25.0 mL at a temperature of 127°C and has a pressure of 155.3 kPa. Calculate the molar mass of the gas.

280. Determine the mass of CO_2 gas that has a volume of 7.10 L at a pressure of 1.11 atm and a temperature of 31°C. Hint: Solve the equation for *m*, and calculate the molar mass using the chemical formula and the periodic table.

281. What is the density of silicon tetrafluoride gas at 72°C and a pressure of 144.5 kPa?

282. At what temperature will nitrogen gas have a density of 1.13 g/L at a pressure of 1.09 atm?

Mixed Review

283. Use the ideal-gas-law equation to calculate the unknown quantity in each of the following sets of measurements.

P	*V*	*n*	*t*
a. 0.0477 atm	15 200 L	? mol	−15°C
b. ? kPa	0.119 mL	0.000 350 mol	0°C
c. 500.0 kPa	250. mL	0.120 mol	?°C
d. 19.5 atm	?	4.7×10^4 mol	300.°C

284. Use the ideal-gas-law equation to calculate the unknown quantity in each of the following sets of measurements.

P	*V*	*m*	*M*	*t*
a. 0.955 atm	3.77 L	8.23 g	? g/mol	25°C
b. 105.0 kPa	50.0 mL	? g	48.02 g/mol	0°C
c. 0.782 atm	? L	3.20×10^{-3} g	2.02 g/mol	−5°C
d. ? atm	2.00 L	7.19 g	159.8 g/mol	185°C
e. 107.2 kPa	26.1 mL	0.414 g	? g/mol	45°C

285. Determine the volume of one mole of an ideal gas at 25°C and 0.915 kPa.

286. Calculate the unknown quantity in each of the following sets of measurements.

P	*Molar Mass*	*Density*	*t*
a. 1.12 atm	? g/mol	2.40 g/L	2°C
b. 7.50 atm	30.07 g/mol	? g/L	20.°C
c. 97.4 kPa	104.09 g/mol	4.37 g/L	? °C
d. ? atm	77.95 g/mol	6.27 g/L	66°C

287. What pressure in atmospheres will 1.36 kg of N_2O gas exert when it is compressed in a 25.0 L cylinder and is stored in an outdoor shed where the temperature can reach 59°C during the summer?

288. Aluminum chloride sublimes at high temperatures. What density will the vapor have at 225°C and 0.939 atm pressure?

289. An unknown gas has a density of 0.0262 g/mL at a pressure of 0.918 atm and a temperature of 10.°C. What is the molar mass of the gas?

290. A large balloon contains 11.7 g of helium. What volume will the helium occupy at an altitude of 10 000 m, where the atmospheric pressure is 0.262 atm and the temperature is −50.°C?

291. A student collects ethane by water displacement at a temperature of 15°C (vapor pressure of water is 1.5988 kPa) and a total pressure of 100.0 kPa. The volume of the collection bottle is 245 mL. How many moles of ethane are in the bottle?

292. A reaction yields 3.75 L of nitrogen monoxide. The volume is measured at 19°C and at a pressure of 1.10 atm. What mass of NO was produced by the reaction?

293. A reaction has a theoretical yield of 8.83 g of ammonia. The reaction gives off 10.24 L of ammonia measured at 52°C and 105.3 kPa. What was the percent yield of the reaction?

294. An unknown gas has a density of 0.405 g/L at a pressure of 0.889 atm and a temperature of 7°C. Calculate its molar mass.

295. A paper label has been lost from an old tank of compressed gas. To help identify the unknown gas, you

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must calculate its molar mass. It is known that the tank has a capacity of 90.0 L and weighs 39.2 kg when empty. You find its current mass to be 50.5 kg. The gauge shows a pressure of 1780 kPa when the temperature is 18°C. What is the molar mass of the gas in the cylinder?

296. What is the pressure inside a tank that has a volume of 1.20×10^3 L and contains 12.0 kg of HCl gas at a temperature of 18°C?

297. What pressure in kPa is exerted at a temperature of 20.°C by compressed neon gas that has a density of 2.70 g/L?

298. A tank with a volume of 658 mL contains 1.50 g of neon gas. The maximum safe pressure that the tank can withstand is 4.50×10^2 kPa. At what temperature will the tank have that pressure?

299. The atmospheric pressure on Mars is about 6.75 millibars (1 bar = 100 kPa = 0.9869 atm), and the nighttime temperature can be about −75°C on the same day that the daytime temperature goes up to −8°C. What volume would a bag containing 1.00 g of H_2 gas have at both the daytime and nighttime temperatures?

300. What is the pressure in kPa of 3.95 mol of Cl_2 gas if it is compressed in a cylinder with a volume of 850. mL at a temperature of 15°C?

301. What volume in mL will 0.00660 mol of hydrogen gas occupy at a pressure of 0.907 atm and a temperature of 9°C?

302. What volume will 8.47 kg of sulfur dioxide gas occupy at a pressure of 89.4 kPa and a temperature of 40.°C?

303. A cylinder contains 908 g of compressed helium. It is to be used to inflate a balloon to a final pressure of 128.3 kPa at a temperature of 2°C. What will the volume of the balloon be under these conditions?

304. The density of dry air at 27°C and 100.0 kPa is 1.162 g/L. Use this information to calculate the molar mass of air (calculate as if air were a pure substance).

Stoichiometry of Gases, Section 11-3

305. In one method of manufacturing nitric acid, ammonia is oxidized to nitrogen monoxide and water:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

What volume of oxygen will be used in a reaction of 2800 L of NH_3? What volume of NO will be produced? All volumes are measured under the same conditions.

306. Fluorine gas reacts violently with water to produce hydrogen fluoride and ozone according to the following equation:

$$3F_2(g) + 3H_2O(l) \rightarrow 6HF(g) + O_3(g)$$

What volumes of O_3 and HF gas would be produced by the complete reaction of 3.60×10^4 mL of fluorine gas? All gases are measured under the same conditions.

307. A sample of ethanol burns in O_2 to form CO_2 and H_2O according to the following equation:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

If the combustion uses 55.8 mL of oxygen measured at 2.26 atm and 40.°C, what volume of CO_2 is produced when measured at STP?

308. Dinitrogen pentoxide decomposes into nitrogen dioxide and oxygen. If 5.00 L of N_2O_5 reacts at STP, what volume of NO_2 is produced when measured at 64.5°C and 1.76 atm?

309. Complete the table below using the following equation, which represents a reaction that produces aluminum chloride:

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

Mass Al	*Volume Cl_2*	*Conditions*	*Mass $AlCl_3$*
a. excess	? L	STP	7.15 g
b. 19.4 g	? L	STP	NA
c. 1.559 kg	? L	20.°C and 0.945 atm	NA
d. excess	920. L	STP	? g
e. ? g	1.049 mL	37°C and 5.00 atm	NA
f. 500.00 kg	? m^3	15°C and 83.0 kPa	NA

Mixed Review

310. The industrial production of ammonia proceeds according to the following equation:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

a. What volume of nitrogen at STP is needed to react with 57.0 mL of hydrogen measured at STP?
b. What volume of NH_3 at STP can be produced from the complete reaction of 6.39×10^4 L of hydrogen?
c. If 20.0 mol of nitrogen is available, what volume of NH_3 at STP can be produced?
d. What volume of H_2 at STP will be needed to produce 800. L of ammonia, measured at 55°C and 0.900 atm?

311. Propane burns according to the following equation:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

a. What volume of water vapor measured at 250.°C and 1.00 atm is produced when 3.0 L of propane at STP is burned?
b. What volume of oxygen at 20.°C and 102.6 kPa is used if 640. L of CO_2 is produced? The CO_2 is also measured at 20.°C and 102.6 kPa.
c. If 465 mL of oxygen at STP is used in the reaction, what volume of CO_2, measured at 37°C and 0.973 atm, is produced?
d. When 2.50 L of C_3H_8 at STP burns, what total volume of gaseous products is formed? The volume of the products is measured at 175°C and 1.14 atm.

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312. Carbon monoxide will burn in air to produce CO_2 according to the following equation:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

What volume of oxygen at STP will be needed to react with 3500. L of CO measured at 20.°C and a pressure of 0.953 atm?

313. Silicon tetrafluoride gas can be produced by the action of HF on silica according to the following equation:

$$SiO_2(s) + 4HF(g) \rightarrow SiF_4(g) + 2H_2O(l)$$

1.00 L of HF gas under pressure at 3.48 atm and a temperature of 25°C reacts completely with SiO_2 to form SiF_4. What volume of SiF_4, measured at 15°C and 0.940 atm, is produced by this reaction?

314. One method used in the eighteenth century to generate hydrogen was to pass steam through red-hot steel tubes. The following reaction takes place:

$$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

a. What volume of hydrogen at STP can be produced by the reaction of 6.28 g of iron?
b. What mass of iron will react with 500. L of steam at 250.°C and 1.00 atm pressure?
c. If 285 g of Fe_3O_4 are formed, what volume of hydrogen, measured at 20.°C and 1.06 atm, is produced?

315. Sodium reacts vigorously with water to produce hydrogen and sodium hydroxide according to the following equation:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

If 0.027 g of sodium reacts with excess water, what volume of hydrogen at STP is formed?

316. Diethyl ether burns in air according to the following equation:

$$C_4H_{10}O(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

If 7.15 L of CO_2 is produced at a temperature of 125°C and a pressure of 1.02 atm, what volume of oxygen, measured at STP, was consumed and what mass of diethyl ether was burned?

317. When nitroglycerin detonates, it produces large volumes of hot gases almost instantly according to the following equation:

$$4C_3H_5N_3O_9(l) \rightarrow 6N_2(g) + 12CO_2(g) + 10H_2O(g) + O_2(g)$$

a. When 0.100 mol of nitroglycerin explodes, what volume of each gas measured at STP is produced?
b. What total volume of gases is produced at 300.°C and 1.00 atm when 10.0 g of nitroglycerin explodes?

318. Dinitrogen monoxide can be prepared by heating ammonium nitrate, which decomposes according to the following equation:

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$

What mass of ammonium nitrate should be decomposed in order to produce 250. mL of N_2O, measured at STP?

319. Phosphine, PH_3, is the phosphorus analogue to ammonia, NH_3. It can be produced by the reaction between calcium phosphide and water according to the following equation:

$$Ca_3P_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(s \text{ and } aq) + 2PH_3(g)$$

What volume of phosphine, measured at 18°C and 102.4 kPa, is produced by the reaction of 8.46 g of Ca_3P_2?

320. In one method of producing aluminum chloride, HCl gas is passed over aluminum and the following reaction takes place:

$$2Al(s) + 6HCl(g) \rightarrow 2AlCl_3(g) + 3H_2(g)$$

What mass of Al should be on hand in order to produce 6.0×10^3 kg of $AlCl_3$? What volume of compressed HCl at 4.71 atm and a temperature of 43°C should be on hand at the same time?

321. Urea, $(NH_2)_2CO$, is an important fertilizer that is manufactured by the following reaction:

$$2NH_3(g) + CO_2(g) \rightarrow (NH_2)_2CO(s) + H_2O(g)$$

What volume of NH_3 at STP will be needed to produce 8.50×10^4 kg of urea if there is an 89.5% yield in the process?

322. An obsolete method of generating oxygen in the laboratory involves the decomposition of barium peroxide by the following equation:

$$2BaO_2(s) \rightarrow 2BaO(s) + O_2(g)$$

What mass of BaO_2 reacted if 265 mL of O_2 is collected by water displacement at 0.975 atm and 10.°C?

323. It is possible to generate chlorine gas by dripping concentrated HCl solution onto solid potassium permanganate according to the following equation:

$$2KMnO_4(aq) + 16HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$$

If excess HCl is dripped onto 15.0 g of $KMnO_4$, what volume of Cl_2 will be produced? The Cl_2 is measured at 15°C and 0.959 atm.

324. Ammonia can be oxidized in the presence of a platinum catalyst according to the following equation:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

The NO that is produced reacts almost immediately with additional oxygen according to the following equation:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

If 35.0 kL of oxygen at STP react in the first reaction, what volume of NH_3 at STP reacts with it? What volume of NO_2 at STP will be formed in the second reaction, assuming there is excess oxygen that was not used up in the first reaction?

325. Oxygen can be generated in the laboratory by heating potassium chlorate. The reaction is represented by the following equation:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

What mass of $KClO_3$ must be used in order to generate 5.00 L of O_2, measured at STP?

326. One of the reactions in the Solvay process is used to make sodium hydrogen carbonate. It occurs when car-

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bon dioxide and ammonia are passed through concentrated salt brine. The following equation represents the reaction:

$$NaCl(aq) + H_2O(l) + CO_2(g) + NH_3(g) \rightarrow NaHCO_3(s) + NH_4Cl(aq)$$

a. What volume of NH_3 at 25°C and 1.00 atm pressure will be required if 38 000 L of CO_2, measured under the same conditions, react to form $NaHCO_3$?
b. What mass of $NaHCO_3$ can be formed when the gases in (a) react with NaCl?
c. If this reaction forms 46.0 kg of $NaHCO_3$, what volume of NH_3, measured at STP, reacted?
d. What volume of CO_2, compressed in a tank at 5.50 atm and a temperature of 42°C, will be needed to produce 100.00 kg of $NaHCO_3$?

327. The combustion of butane is represented in the following equation:

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

a. If 4.74 g of butane react with excess oxygen, what volume of CO_2, measured at 150.°C and 1.14 atm, will be formed?
b. What volume of oxygen, measured at 0.980 atm and 75°C, will be consumed by the complete combustion of 0.500 g of butane?
c. A butane-fueled torch has a mass of 876.2 g. After burning for some time, the torch has a mass of 859.3 g. What volume of CO_2, at STP, was formed while the torch burned?
d. What mass of H_2O is produced when butane burns and produces 3720 L of CO_2, measured at 35°C and 0.993 atm pressure?

Concentration of Solutions, Section 13-3

Percentage Concentration

328. What is the percentage concentration of 75.0 g of ethanol dissolved in 500.0 g of water?

329. A chemist dissolves 3.50 g of potassium iodate and 6.23 g of potassium hydroxide in 805.05 g of water. What is the percentage concentration of each solute in the solution?

330. A student wants to make a 5.00% solution of rubidium chloride using 0.377 g of the substance. What mass of water will be needed to make the solution?

331. What mass of lithium nitrate would have to be dissolved in 30.0 g of water in order to make an 18.0% solution?

Molarity

332. Determine the molarity of a solution prepared by dissolving 141.6 g of citric acid, $C_3H_5O(COOH)_3$, in water and then diluting the resulting solution to 3500.0 mL.

333. What is the molarity of a salt solution made by dissolving 280.0 mg of NaCl in 2.00 mL of water? Assume the final volume is the same as the volume of the water.

334. What is the molarity of a solution that contains 390.0 g of acetic acid, CH_3COOH, dissolved in enough acetone to make 1000.0 mL of solution?

335. What mass of glucose, $C_6H_{12}O_6$, would be required to prepare 5.000×10^3 L of a 0.215 M solution?

336. What mass of magnesium bromide would be required to prepare 720. mL of a 0.0939 M aqueous solution?

337. What mass of ammonium chloride is dissolved in 300. mL of a 0.875 M solution?

Molality

338. Determine the molality of a solution of 560 g of acetone, CH_3COCH_3, in 620 g of water.

339. What is the molality of a solution of 12.9 g of fructose, $C_6H_{12}O_6$, in 31.0 g of water?

340. How many moles of 2-butanol, $CH_3CHOHCH_2CH_3$, must be dissolved in 125 g of ethanol in order to produce a 12.0 *m* 2-butanol solution? What mass of 2-butanol is this?

Mixed Review

341. Complete the table below by determining the missing quantity in each example. All solutions are aqueous. Any quantity that is not applicable to a given solution is marked NA.

Solution Made	*Mass of Solute Used*	*Quantity of Solution Made*	*Quantity of Solvent Used*
a. 12.0% $KMnO_4$	? g $KMnO_4$	500.0 g	? g H_2O
b. 0.60 M $BaCl_2$	? g $BaCl_2$	1.750 L	NA
c. 6.20 *m* glycerol, $HOCH_2CHOHCH_2OH$	? g glycerol	NA	800.0 g H_2O
d. ? M $K_2Cr_2O_7$	12.27 g $K_2Cr_2O_7$	650. mL	NA
e. ? *m* $CaCl_2$	288 g $CaCl_2$	NA	2.04 kg H_2O
f. 0.160 M NaCl	? g NaCl	25.0 mL	NA
g. 2.00 *m* glucose, $C_6H_{12}O_6$	? g glucose	? g solution	1.50 kg H_2O

342. How many moles of H_2SO_4 are in 2.50 L of a 4.25 M aqueous solution?

343. Determine the molal concentration of 71.5 g of linoleic acid, $C_{18}H_{32}O_2$, in 525 g of hexane, C_6H_{14}.

344. You have a solution that is 16.2% sodium thiosulfate, $Na_2S_2O_3$, by mass.
a. What mass of sodium thiosulfate is in 80.0 g of solution?
b. How many moles of sodium thiosulfate are in 80.0 g of solution?
c. If 80.0 g of the sodium thiosulfate solution is diluted to 250.0 mL with water, what is the molarity of the resulting solution?

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345. What mass of anhydrous cobalt(II) chloride would be needed in order to make 650.00 mL of a 4.00 M cobalt(II) chloride solution?

346. A student wants to make a 0.150 M aqueous solution of silver nitrate, $AgNO_3$, and has a bottle containing 11.27 g of silver nitrate. What should be the final volume of the solution?

347. What mass of urea, NH_2CONH_2, must be dissolved in 2250 g of water in order to prepare a 1.50 *m* solution?

348. What mass of barium nitrate is dissolved in 21.29 mL of a 3.38 M solution?

349. Describe what you would do to prepare 100.0 g of a 3.5% solution of ammonium sulfate in water.

350. What mass of anhydrous calcium chloride should be dissolved in 590.0 g of water in order to produce a 0.82 *m* solution?

351. How many moles of ammonia are in 0.250 L of a 5.00 M aqueous ammonia solution? If this solution were diluted to 1.000 L, what would be the molarity of the resulting solution?

352. What is the molar mass of a solute if 62.0 g of the solute in 125 g of water produce a 5.3 *m* solution?

353. A saline solution is 0.9% NaCl. What masses of NaCl and water would be required to prepare 50. L of this saline solution? Assume that the density of water is 1.000 g/mL and that the NaCl does not add to the volume of the solution.

354. A student weighs an empty beaker on a balance and finds its mass to be 68.60 g. The student weighs the beaker again after adding water and finds the new mass to be 115.12 g. A mass of 4.08 g of glucose is then dissolved in the water. What is the percentage concentration of glucose in the solution?

355. The density of ethyl acetate at 20°C is 0.902 g/mL. What volume of ethyl acetate at 20°C would be required to prepare a 2.0% solution of cellulose nitrate using 25 g of cellulose nitrate?

356. Aqueous cadmium chloride reacts with sodium sulfide to produce bright-yellow cadmium sulfide. Write the balanced equation for this reaction and answer the following questions.
- **a.** How many moles of $CdCl_2$ are in 50.00 mL of a 3.91 M solution?
- **b.** If the solution in (a) reacted with excess sodium sulfide, how many moles of CdS would be formed?
- **c.** What mass of CdS would be formed?

357. What mass of H_2SO_4 is contained in 60.00 mL of a 5.85 M solution of sulfuric acid?

358. A truck carrying 22.5 kL of 6.83 M aqueous hydrochloric acid used to clean brick and masonry has overturned. The authorities plan to neutralize the acid with sodium carbonate. How many moles of HCl will have to be neutralized?

359. A chemist wants to produce 12.00 g of barium sulfate by reacting a 0.600 M $BaCl_2$ solution with excess H_2SO_4, as shown in the reaction below. What volume of the $BaCl_2$ solution should be used?

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

360. Many substances are hydrates. Whenever you make a solution, it is important to know whether or not the solute you are using is a hydrate and, if it is a hydrate, how many molecules of water are present per formula unit of the substance. This water must be taken into account when weighing out the solute. Something else to remember when making aqueous solutions from hydrates is that once the hydrate is dissolved, the water of hydration is considered to be part of the solvent. A common hydrate used in the chemistry laboratory is copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$. Describe how you would make each of the following solutions using $CuSO_4 \cdot 5H_2O$. Specify masses and volumes as needed.
- **a.** 100. g of a 6.00% solution of $CuSO_4$
- **b.** 1.00 L of a 0.800 M solution of $CuSO_4$
- **c.** a 3.5 *m* solution of $CuSO_4$ in 1.0 kg of water

361. What mass of calcium chloride hexahydrate is required in order to make 700.0 mL of a 2.50 M solution?

362. What mass of the amino acid arginine, $C_6H_{14}N_4O_2$, would be required to make 1.250 L of a 0.00205 M solution?

363. How much water would you have to add to 2.402 kg of nickel(II) sulfate hexahydrate in order to prepare a 25.00% solution?

364. What mass of potassium aluminum sulfate dodecahydrate, $KAl(SO_4)_2 \cdot 12H_2O$, would be needed to prepare 35.00 g of a 15.00% $KAl(SO_4)_2$ solution? What mass of water would be added to make this solution?

Dilutions, Section 13-3

365. Complete the table below by calculating the missing value in each row.

Molarity of Stock Solution	*Volume of Stock Solution*	*Molarity of Dilute Solution*	*Volume of Dilute Solution*
a. 0.500 M KBr	20.00 mL	? M KBr	100.00 mL
b. 1.00 M LiOH	? mL	0.075 M LiOH	500.00 mL
c. ? M HI	5.00 mL	0.0493 M HI	100.00 mL
d. 12.0 M HCl	0.250 L	1.8 M HCl	? L
e. 7.44 M NH_3	? mL	0.093 M NH_3	4.00 L

366. What volume of water would be added to 16.5 mL of a 0.0813 M solution of sodium borate in order to get a 0.0200 M solution?

Mixed Review

367. What is the molarity of a solution of ammonium chloride prepared by diluting 50.00 mL of a 3.79 M NH_4Cl solution to 2.00 L?

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368. A student takes a sample of KOH solution and dilutes it with 100.00 mL of water. The student determines that the diluted solution is 0.046 M KOH, but has forgotten to record the volume of the original sample. The concentration of the original solution is 2.09 M. What was the volume of the original sample?

369. A chemist wants to prepare a stock solution of H_2SO_4 so that samples of 20.00 mL will produce a solution with a concentration of 0.50 M when added to 100.0 mL of water.
- **a.** What should the molarity of the stock solution be?
- **b.** If the chemist wants to prepare 5.00 L of the stock solution from concentrated H_2SO_4, which is 18.0 M, what volume of concentrated acid should be used?
- **c.** The density of 18.0 M H_2SO_4 is 1.84 g/mL. What mass of concentrated H_2SO_4 should be used to make the stock solution in (b)?

370. To what volume should 1.19 mL of an 8.00 M acetic acid solution be diluted in order to obtain a final solution that is 1.50 M?

371. What volume of a 5.75 M formic acid solution should be used to prepare 2.00 L of a 1.00 M formic acid solution?

372. A 25.00 mL sample of ammonium nitrate solution produces a 0.186 M solution when diluted with 50.00 mL of water. What is the molarity of the stock solution?

373. Given a solution of known percentage concentration by mass, a laboratory worker can often measure out a calculated mass of the solution in order to obtain a certain mass of solute. Sometimes, though, it is impractical to use the mass of a solution, especially with fuming solutions, such as concentrated HCl and concentrated HNO_3. Measuring these solutions by volume is much more practical. In order to determine the volume that should be measured, a worker would need to know the density of the solution. This information usually appears on the label of the solution bottle.
- **a.** Concentrated hydrochloric acid is 36% HCl by mass and has a density of 1.18 g/mL. What is the volume of 1.0 kg of this HCl solution? What volume contains 1.0 g of HCl? What volume contains 1.0 mol of HCl?
- **b.** The density of concentrated nitric acid is 1.42 g/mL, and its concentration is 71% HNO_3 by mass. What volume of concentrated HNO_3 would be needed to prepare 10.0 L of a 2.00 M solution of HNO_3?
- **c.** What volume of concentrated HCl solution would be needed to prepare 4.50 L of 3.0 M HCl? See (a) for data.

374. A 3.8 M solution of $FeSO_4$ solution is diluted to eight times its original volume. What is the molarity of the diluted solution?

375. A chemist prepares 480. mL of a 2.50 M solution of $K_2Cr_2O_7$ in water. A week later, the chemist wants to use the solution, but the stopper has been left off the flask and 39 mL of water has evaporated. What is the new molarity of the solution?

376. You must write out procedures for a group of lab technicians. One test they will perform requires 25.00 mL of a 1.22 M solution of acetic acid. You decide to use a 6.45 M acetic acid solution that you have on hand. What procedure should the technicians use in order to get the solution they need?

377. A chemical test has determined the concentration of a solution of an unknown substance to be 2.41 M. A 100.0 mL volume of the solution is evaporated to dryness, leaving 9.56 g of crystals of the unknown solute. Calculate the molar mass of the unknown substance.

378. Tincture of iodine can be prepared by dissolving 34 g of I_2 and 25 g of KI in 25 mL of distilled water and diluting the solution to 500. mL with ethanol. What is the molarity of I_2 in the solution?

379. Phosphoric acid is commonly supplied as an 85% solution. What mass of this solution would be required to prepare 600.0 mL of a 2.80 M phosphoric acid solution?

380. Commercially available concentrated sulfuric acid is 18.0 M H_2SO_4. What volume of concentrated H_2SO_4 would you use in order to make 3.00 L of a 4.0 M stock solution?

381. Describe how to prepare 1.00 L of a 0.495 M solution of urea, NH_2CONH_2, starting with a 3.07 M stock solution.

382. Honey is a solution consisting almost entirely of a mixture of the hexose sugars fructose and glucose; both sugars have the formula $C_6H_{12}O_6$, but they differ in molecular structure.
- **a.** A sample of honey is found to be 76.2% $C_6H_{12}O_6$ by mass. What is the molality of the hexose sugars in honey? Consider the sugars to be equivalent.
- **b.** The density of the honey sample is 1.42 g/mL. What mass of hexose sugars are in 1.00 L of honey? What is the molarity of the mixed hexose sugars in honey?

383. Industrial chemicals used in manufacturing are almost never pure, and the content of the material may vary from one batch to the next. For these reasons, a sample is taken from each shipment and sent to a laboratory, where its makeup is determined. This procedure is called assaying. Once the content of a material is known, engineers adjust the manufacturing process to account for the degree of purity of the starting chemicals.

Suppose you have just received a shipment of sodium carbonate, Na_2CO_3. You weigh out 50.00 g of the material, dissolve it in water, and dilute the solution to 1.000 L. You remove 10.00 mL from the solution and dilute it to 50.00 mL. By measuring the amount of a second substance that reacts with Na_2CO_3, you determine that the concentration of sodium carbonate in the diluted solution is 0.0890 M. Calculate the percentage of Na_2CO_3 in the original batch of material. The molar mass of Na_2CO_3 is 105.99 g. (Hint: Determine the number of moles in the original solution and convert to mass of Na_2CO_3.)

384. A student wants to prepare 0.600 L of a stock solution of copper(II) chloride so that 20.0 mL of the stock solution diluted by adding 130.0 mL of water will yield

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a 0.250 M solution. What mass of $CuCl_2$ should be used to make the stock solution?

385. You have a bottle containing a 2.15 M $BaCl_2$ solution. You must tell other students how to dilute this solution to get various volumes of a 0.65 M $BaCl_2$ solution. By what factor will you tell them to dilute the stock solution? In other words, when a student removes any volume, V, of the stock solution, how many times V of water should be added to dilute to 0.65 M?

386. You have a bottle containing an 18.2% solution of strontium nitrate (density = 1.02 g/mL).
- **a.** What mass of strontium nitrate is dissolved in 80.0 mL of this solution?
- **b.** How many moles of strontium nitrate are dissolved in 80.0 mL of the solution?
- **c.** If 80.0 mL of this solution is diluted with 420.0 mL of water, what is the molarity of the solution?

Colligative Properties, Section 14-2

387. Determine the freezing point of a solution of 60.0 g of glucose, $C_6H_{12}O_6$, dissolved in 80.0 g of water.

388. What is the freezing point of a solution of 645 g of urea, H_2NCONH_2, dissolved in 980. g of water?

389. What is the expected boiling point of a brine solution containing 30.00 g of KBr dissolved in 100.00 g of water?

390. What is the expected boiling point of a $CaCl_2$ solution containing 385 g of $CaCl_2$ dissolved in 1.230×10^3 g of water?

391. A solution of 0.827 g of an unknown non-electrolyte compound in 2.500 g of water has a freezing point of −10.18°C. Calculate the molar mass of the compound.

392. A 0.171 g sample of an unknown organic compound is dissolved in ether. The solution has a total mass of 2.470 g. The boiling point of the solution is found to be 36.43°C. What is the molar mass of the organic compound?

Mixed Review

In each of the following problems, assume that the solute is a nonelectrolyte unless otherwise stated.

393. Calculate the freezing point and boiling point of a solution of 383 g of glucose dissolved in 400. g of water.

394. Determine the boiling point of a solution of 72.4 g of glycerol dissolved in 122.5 g of water.

395. What is the boiling point of a solution of 30.20 g of ethylene glycol, $HOCH_2CH_2OH$, in 88.40 g of phenol?

396. What mass of ethanol, CH_3CH_2OH, should be dissolved in 450. g of water to obtain a freezing point of −4.5°C?

397. Calculate the molar mass of a nonelectrolyte that lowers the freezing point of 25.00 g of water to −3.9°C when 4.27 g of the substance is dissolved in the water.

398. What is the freezing point of a solution of 1.17 g of 1-naphthol, $C_{10}H_8O$, dissolved in 2.00 mL of benzene at 20°C? The density of benzene at 20°C is 0.876 g/mL. K_f for benzene is −5.12°C/*m*, and benzene's normal freezing point is 5.53°C.

399. The boiling point of a solution containing 10.44 g of an unknown nonelectrolyte in 50.00 g of acetic acid is 159.2°C. What is the molar mass of the solute?

400. A 0.0355 g sample of an unknown molecular compound is dissolved in 1.000 g of liquid camphor at 200.0°C. Upon cooling, the camphor freezes at 157.7°C. Calculate the molar mass of the unknown compound.

401. Determine the boiling point of a solution of 22.5 g of fructose, $C_6H_{12}O_6$, in 294 g of phenol.

402. Ethylene glycol, $HOCH_2CH_2OH$, is effective as an antifreeze, but it also raises the boiling temperature of automobile coolant, which helps prevent loss of coolant when the weather is hot.
- **a.** What is the freezing point of a 50.0% solution of ethylene glycol in water?
- **b.** What is the boiling point of the same 50.0% solution?

403. The value of K_f for cyclohexane is −20.0°C/*m*, and its normal freezing point is 6.6°C. A mass of 1.604 g of a waxy solid dissolved in 10.000 g of cyclohexane results in a freezing point of −4.4°C. Calculate the molar mass of the solid.

404. What is the expected freezing point of an aqueous solution of 2.62 kg of nitric acid, HNO_3, in a solution with a total mass of 5.91 kg? Assume that the nitric acid is completely ionized.

405. An unknown organic compound is mixed with 0.5190 g of naphthalene crystals to give a mixture having a total mass of 0.5959 g. The mixture is heated until the naphthalene melts and the unknown substance dissolves. Upon cooling, the solution freezes at a temperature of 74.8°C. What is the molar mass of the unknown compound?

406. What is the boiling point of a solution of 8.69 g of the electrolyte sodium acetate, $NaCH_3COO$, dissolved in 15.00 g of water?

407. What is the expected freezing point of a solution of 110.5 g of H_2SO_4 in 225 g of water? Assume sulfuric acid completely dissociates in water.

408. A compound called pyrene has the empirical formula C_8H_5. When 4.04 g of pyrene is dissolved in 10.00 g of benzene, the boiling point of the solution is 85.1°C. Calculate the molar mass of pyrene and determine its molecular formula. The molal boiling-point constant for benzene is 2.53°C/*m*. Its normal boiling point is 80.1°C.

409. What mass of $CaCl_2$, when dissolved in 100.00 g of water, gives an expected freezing point of −5.0°C; $CaCl_2$ is ionic? What mass of glucose would give the same result?

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410. A compound has the empirical formula CH_2O. When 0.0866 g is dissolved in 1.000 g of ether, the solution's boiling point is 36.5°C. Determine the molecular formula of this substance.

411. What is the freezing point of a 28.6% (by mass) aqueous solution of HCl? Assume the HCl is 100% ionized.

412. What mass of ethylene glycol, $HOCH_2CH_2OH$, must be dissolved in 4.510 kg of water to result in a freezing point of −18.0°C? What is the boiling point of the same solution?

413. A water solution containing 2.00 g of an unknown molecular substance dissolved in 10.00 g of water has a freezing point of −4.0°C.
- **a.** Calculate the molality of the solution.
- **b.** When 2.00 g of the substance is dissolved in acetone instead of in water, the boiling point of the solution is 58.9°C. The normal boiling point of acetone is 56.00°C, and its K_b is 1.71°C/*m*. Calculate the molality of the solution from this data.

414. A chemist wants to prepare a solution with a freezing point of −22.0°C and has 100.00 g of glycerol on hand. What mass of water should the chemist mix with the glycerol?

415. An unknown carbohydrate compound has the empirical formula CH_2O. A solution consisting of 0.515 g of the carbohydrate dissolved in 1.717 g of acetic acid freezes at 8.8°C. What is the molar mass of the carbohydrate? What is its molecular formula?

416. An unknown organic compound has the empirical formula C_2H_2O. A solution of 3.775 g of the unknown compound dissolved in 12.00 g of water is cooled until it freezes at a temperature of −4.72°C. Determine the molar mass and the molecular formula of the compound.

pH, Section 16-1

417. The hydroxide ion concentration of an aqueous solution is 6.4×10^{-5} M. What is the hydronium ion concentration?

418. Calculate the H_3O^+ and OH^- concentrations in a 7.50×10^{-4} M solution of HNO_3, a strong acid.

419. Determine the pH of a 0.001 18 M solution of HBr.

420.
- **a.** What is the pH of a solution that has a hydronium ion concentration of 1.0 M?
- **b.** What is the pH of a 2.0 M solution of HCl, assuming the acid remains 100% ionized?
- **c.** What is the theoretical pH of a 10. M solution of HCl?

421. What is the pH of a solution with the following hydroxide ion concentrations?
- **a.** 1×10^{-5} M
- **b.** 5×10^{-8} M
- **c.** 2.90×10^{-11} M

422. What are the pOH and hydroxide ion concentration of a solution with a pH of 8.92?

423. What are the pOH values of solutions with the following hydronium ion concentrations?
- **a.** 2.51×10^{-13} M
- **b.** 4.3×10^{-3} M
- **c.** 9.1×10^{-6} M
- **d.** 0.070 M

424. A solution is prepared by dissolving 3.50 g of sodium hydroxide in water and adding water until the total volume of the solution is 2.50 L. What are the OH^- and H_3O^+ concentrations?

425. If 1.00 L of a potassium hydroxide solution with a pH of 12.90 is diluted to 2.00 L, what is the pH of the resulting solution?

Mixed Review

426. Calculate the H_3O^+ and OH^- concentrations in the following solutions. Each is either a strong acid or a strong base.
- **a.** 0.05 M sodium hydroxide
- **b.** 0.0025 M sulfuric acid
- **c.** 0.013 M lithium hydroxide
- **d.** 0.150 M nitric acid
- **e.** 0.0200 M calcium hydroxide
- **f.** 0.390 M perchloric acid

427. What is the pH of each solution in item 426?

428. Calculate $[H_3O^+]$ and $[OH^-]$ in a 0.160 M solution of potassium hydroxide. Assume that the solute is 100% dissociated at this concentration.

429. The pH of an aqueous solution of NaOH is 12.9. What is the molarity of the solution?

430. What is the pH of a 0.001 25 M HBr solution? If 175 mL of this solution is diluted to a total volume of 3.00 L, what is the pH of the diluted solution?

431. What is the pH of a 0.0001 M solution of NaOH? What is the pH of a 0.0005 M solution of NaOH?

432. A solution is prepared using 15.0 mL of 1.0 M HCl and 20.0 mL of 0.50 M HNO_3. The final volume of the solution is 1.25 L. Answer the following questions:
- **a.** What are the $[H_3O^+]$ and $[OH^-]$ in the final solution?
- **b.** What is the pH of the final solution?

433. A container is labeled 500.0 mL of 0.001 57 M nitric acid solution. A chemist finds that the container was not sealed and that some evaporation has taken place. The volume of solution is now 447.0 mL.
- **a.** What was the original pH of the solution?
- **b.** What is the pH of the solution now?

434. Calculate the hydroxide ion concentration in an aqueous solution that has a 0.000 35 M hydronium ion concentration.

435. A solution of sodium hydroxide has a pH of 12.14. If 50.00 mL of the solution is diluted to 2.000 L with water, what is the pH of the diluted solution?

436. An acetic acid solution has a pH of 4.0. What are the $[H_3O^+]$ and $[OH^-]$ in this solution?

437. What is the pH of a 0.000 460 M solution of $Ca(OH)_2$?

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438. A solution of strontium hydroxide with a pH of 11.4 is to be prepared. What mass of strontium hydroxide would be required to make 1.00 L of this solution?

439. A solution of NH_3 has a pH of 11.00. What are the concentrations of hydronium and hydroxide ions in this solution?

440. Acetic acid does not completely ionize in solution. Percent ionization of a substance dissolved in water is equal to the moles of ions produced as a percentage of the moles of ions that would be produced if the substance were completely ionized. Calculate the percent ionization of acetic acid in the following solutions.
a. 1.0 M acetic acid solution with a pH of 2.40
b. 0.10 M acetic acid solution with a pH of 2.90
c. 0.010 M acetic acid solution with a pH of 3.40

441. Calculate the pH of a solution that contains 5.00 g of HNO_3 in 2.00 L of solution.

442. A solution of HCl has a pH of 1.50. Determine the pH of the solutions made in each of the following ways.
a. 1.00 mL of the solution is diluted to 1000. mL with water.
b. 25.00 mL is diluted to 200. mL with distilled water.
c. 18.83 mL of the solution is diluted to 4.000 L with distilled water.
d. 1.50 L is diluted to 20.0 kL with distilled water.

443. An aqueous solution contains 10 000 times more hydronium ions than hydroxide ions. What is the concentration of each ion?

444. A potassium hydroxide solution has a pH of 12.90. Enough acid is added to react with half of the OH^- ions present. What is the pH of the resulting solution? Assume that the products of the neutralization have no effect on pH and that the amount of additional water produced is negligible.

445. A hydrochloric acid solution has a pH of 1.70. What is the $[H_3O^+]$ in this solution? Considering that HCl is a strong acid, what is the HCl concentration of the solution?

446. What is the molarity of a solution of the strong base $Ca(OH)_2$ in a solution that has a pH of 10.80?

447. You have a 1.00 M solution of the strong acid, HCl. What is the pH of this solution? You need a solution of pH 4.00. To what volume would you dilute 1.00 L of the HCl solution to get this pH? To what volume would you dilute 1.00 L of the pH 4.00 solution to get a solution of pH 6.00? To what volume would you dilute 1.00 L of the pH 4.00 solution to get a solution of pH 8.00?

448. A solution of chloric acid, $HClO_3$, a strong acid, has a pH of 1.28. How many moles of NaOH would be required to react completely with the $HClO_3$ in 1.00 L of the solution? What mass of NaOH is required?

449. A solution of the weak base NH_3 has a pH of 11.90. How many moles of HCl would have to be added to 1.00 L of the ammonia to react with all of the OH^- ions present at pH 11.90?

450. The pH of a citric acid solution is 3.15. What are the $[H_3O^+]$ and $[OH^-]$ in this solution?

Titrations, Section 16-2

In each of the following problems, the acids and bases react in a mole ratio of 1 mol base : 1 mol acid.

451. A student titrates a 20.00 mL sample of a solution of HBr with unknown molarity. The titration requires 20.05 mL of a 0.1819 M solution of NaOH. What is the molarity of the HBr solution?

452. Vinegar can be assayed to determine its acetic acid content. Determine the molarity of acetic acid in a 15.00 mL sample of vinegar that requires 22.70 mL of a 0.550 M solution of NaOH to reach the equivalence point.

453. A 20.00 mL sample of a solution of $Sr(OH)_2$ is titrated to the equivalence point with 43.03 mL of 0.1159 M HCl. What is the molarity of the $Sr(OH)_2$ solution?

454. A 35.00 mL sample of ammonia solution is titrated to the equivalence point with 54.95 mL of a 0.400 M sulfuric acid solution. What is the molarity of the ammonia solution?

In the problems below, assume that impurities are not acidic or basic and that they do not react in an acid-base titration.

455. A supply of glacial acetic acid has absorbed water from the air. It must be assayed to determine the actual percentage of acetic acid. 2.000 g of the acid is diluted to 100.00 mL, and 20.00 mL is titrated with a solution of sodium hydroxide. The base solution has a concentration of 0.218 M, and 28.25 mL is used in the titration. Calculate the percentage of acetic acid in the original sample. Write the titration equation to get the mole ratio.

456. A shipment of crude sodium carbonate must be assayed for its Na_2CO_3 content. You receive a small jar containing a sample from the shipment and weigh out 9.709 g into a flask, where it is dissolved in water and diluted to 1.0000 L with distilled water. A 10.00 mL sample is taken from the flask and titrated to the equivalence point with 16.90 mL of a 0.1022 M HCl solution. Determine the percentage of Na_2CO_3 in the sample. Write the titration equation to get the mole ratio.

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457. A 50.00 mL sample of a potassium hydroxide is titrated with a 0.8186 M HCl solution. The titration requires 27.87 mL of the HCl solution to reach the equivalence point. What is the molarity of the KOH solution?

458. A 15.00 mL sample of acetic acid is titrated with 34.13 mL of 0.9940 M NaOH. Determine the molarity of the acetic acid.

459. A 12.00 mL sample of an ammonia solution is titrated with 1.499 M HNO_3 solution. A total of 19.48 mL of acid is required to reach the equivalence point. What is the molarity of the ammonia solution?

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460. A certain acid and base react in a 1:1 ratio.
- **a.** If the acid and base solutions are of equal concentration, what volume of acid will titrate a 20.00 mL sample of the base?
- **b.** If the acid is twice as concentrated as the base, what volume of acid will be required to titrate 20.00 mL of the base?
- **c.** How much acid will be required if the base is four times as concentrated as the acid, and 20.00 mL of base is used?

461. A 10.00 mL sample of a solution of hydrofluoric acid, HF, is diluted to 500.00 mL. A 20.00 mL sample of the diluted solution requires 13.51 mL of a 0.1500 M NaOH solution to be titrated to the equivalence point. What is the molarity of the original HF solution?

462. A solution of oxalic acid, a diprotic acid, is used to titrate a 16.22 mL sample of a 0.5030 M KOH solution. If the titration requires 18.41 mL of the oxalic acid solution, what is its molarity?

463. A H_2SO_4 solution of unknown molarity is titrated with a 1.209 M NaOH solution. The titration requires 42.27 mL of the NaOH solution to reach the equivalent point with 25.00 mL of the H_2SO_4 solution. What is the molarity of the acid solution?

464. Potassium hydrogen phthalate, $KHC_8H_4O_4$, is a solid acidic substance that reacts in a 1:1 mole ratio with bases that have one hydroxide ion. Suppose that 0.7025 g of potassium hydrogen phthalate is titrated to the equivalence point by 20.18 mL of a KOH solution. What is the molarity of the KOH solution?

465. A solution of citric acid, a triprotic acid, is titrated with a sodium hydroxide solution. A 20.00 mL sample of the citric acid solution requires 17.03 mL of a 2.025 M solution of NaOH to reach the equivalence point. What is the molarity of the acid solution?

466. A flask contains 41.04 mL of a solution of potassium hydroxide. The solution is titrated and reaches an equivalence point when 21.65 mL of a 0.6515 M solution of HNO_3 is added. Calculate the molarity of the base solution.

467. A bottle is labeled 2.00 M H_2SO_4. You decide to titrate a 20.00 mL sample with a 1.85 M NaOH solution. What volume of NaOH solution would you expect to use if the label is correct?

468. What volume of a 0.5200 M solution of H_2SO_4 would be needed to titrate 100.00 mL of a 0.1225 M solution of $Sr(OH)_2$?

469. A sample of a crude grade of KOH is sent to the lab to be tested for KOH content. A 4.005 g sample is dissolved and diluted to 200.00 mL with water. A 25.00 mL sample of the solution is titrated with a 0.4388 M HCl solution and requires 19.93 mL to reach the equivalence point. How many moles of KOH were in the 4.005 g sample? What mass of KOH is this? What is the percent of KOH in the crude material?

470. What mass of magnesium hydroxide would be required for the magnesium hydroxide to react to the equivalence point with 558 mL of 3.18 M hydrochloric acid?

471. An ammonia solution of unknown concentration is titrated with a solution of hydrochloric acid. The HCl solution is 1.25 M, and 5.19 mL are required to titrate 12.61 mL of the ammonia solution. What is the molarity of the ammonia solution?

472. What volume of 2.811 M oxalic acid solution is needed to react to the equivalence point with a 5.090 g sample of material that is 92.10% NaOH? Oxalic acid is a diprotic acid.

473. Standard solutions of accurately known concentration are available in most laboratories. These solutions are used to titrate other solutions to determine their concentrations. Once the concentration of the other solutions are accurately known, they may be used to titrate solutions of unknowns.

The molarity of a solution of HCl is determined by titrating the solution with an accurately known solution of $Ba(OH)_2$, which has a molar concentration of 0.1529 M. A volume of 43.09 mL of the $Ba(OH)_2$ solution titrates 26.06 mL of the acid solution. The acid solution is in turn used to titrate 15.00 mL of a solution of rubidium hydroxide. The titration requires 27.05 mL of the acid.
- **a.** What is the molarity of the HCl solution?
- **b.** What is the molarity of the RbOH solution?

474. A truck containing 2800 kg of a 6.0 M hydrochloric acid has been in an accident and is in danger of spilling its load. What mass of $Ca(OH)_2$ should be sent to the scene in order to neutralize all of the acid in case the tank bursts? The density of the 6.0 M HCl solution is 1.10 g/mL.

475. A 1.00 mL sample of a fairly concentrated nitric acid solution is diluted to 200.00 mL. A 10.00 mL sample of the diluted solution requires 23.94 mL of a 0.0177 M solution of $Ba(OH)_2$ to be titrated to the equivalence point. Determine the molarity of the original nitric acid solution.

476. What volume of 4.494 M H_2SO_4 solution would be required to react to the equivalence point with 7.2280 g of LiOH(*s*)?

Thermochemistry, Sections 17-1; 17-2

477. Calculate the reaction enthalpy for the following reaction:

$$5CO_2(g) + Si_3N_4(s) \rightarrow 3SiO(s) + 2N_2O(g) + 5CO(g)$$

Use the following equations and data:

(1) $CO(g) + SiO_2(s) \rightarrow SiO(g) + CO_2(g)$

(2) $8CO_2(g) + Si_3N_4(s) \rightarrow 3SiO_2(s) + 2N_2O(g) + 8CO(g)$

$\Delta H_{\text{reaction 1}} = +520.9$ kJ

$\Delta H_{\text{reaction 2}} = +461.05$ kJ

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Determine ΔH for each of the following three reactions.

478. The following reaction is used to make CaO from limestone:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

479. The following reaction represents the oxidation of FeO to Fe_2O_3:

$$2FeO(s) + O_2(g) \rightarrow Fe_2O_3(s)$$

480. The following reaction of ammonia and hydrogen fluoride produces ammonium fluoride:

$$NH_3(g) + HF(g) \rightarrow NH_4F(s)$$

481. Calculate the free energy change, ΔG, for the combustion of hydrogen sulfide according to the following chemical equation. Assume reactants and products are at 25°C:

$$H_2S(g) + O_2(g) \rightarrow H_2O(l) + SO_2(g)$$

$\Delta H_{reaction} = -562.1$ kJ/mol

$\Delta S_{reaction} = -0.09278$ kJ/mol•K

482. Calculate the free energy change for the decomposition of sodium chlorate. Assume reactants and products are at 25°C:

$$NaClO_3(s) \rightarrow NaCl(s) + O_2(g)$$

$\Delta H_{reaction} = -19.1$ kJ/mol

$\Delta S_{reaction} = -0.1768$ kJ/mol•K

483. Calculate the free energy change for the combustion of 1 mol of ethane. Assume reactants and products are at 25°C:

$$C_2H_6(g) + O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

$\Delta H_{reaction} = -1561$ kJ/mol

$\Delta S_{reaction} = -0.4084$ kJ/mol•K

Mixed Review

484. Calculate ΔH for the reaction of fluorine with water:

$$F_2(g) + H_2O(l) \rightarrow 2HF(g) + O_2(g)$$

485. Calculate ΔH for the reaction of calcium oxide and sulfur trioxide:

$$CaO(s) + SO_3(g) \rightarrow CaSO_4(s)$$

Use the following equations and data:

$$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(l)$$

$\Delta H = -132.5$ kJ/mol

$$H_2SO_4(l) + Ca(s) \rightarrow CaSO_4(s) + H_2(g)$$

$\Delta H = -602.5$ kJ/mol

$$Ca(s) + O_2(g) \rightarrow CaO(s)$$

$\Delta H = -634.9$ kJ/mol

$$H_2(g) + O_2(g) \rightarrow H_2O(l)$$

$\Delta H = -285.8$ kJ/mol

486. Calculate ΔH for the reaction of sodium oxide with sulfur dioxide:

$$Na_2O(s) + SO_2(g) \rightarrow Na_2SO_3(s)$$

487. Use enthalpies of combustion to calculate ΔH for the oxidation of 1-butanol to make butanoic acid:

$$C_4H_9OH(l) + O_2(g) \rightarrow C_3H_7COOH(l) + H_2O(l)$$

Combustion of butanol:

$$C_4H_9OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

$\Delta H_c = -2675.9$ kJ/mol

Combustion of butanoic acid:

$$C_3H_7COOH(l) + 5O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$$

$\Delta H_c = -2183.6$ kJ/mol

488. Determine the free energy change for the reduction of CuO with hydrogen. Products and reactants are at 25°C.

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

$\Delta H = -128.5$ kJ/mol

$\Delta S = -70.1$ J/mol•K

489. Calculate the enthalpy change at 25°C for the reaction of sodium iodide and chlorine. Use only the data given.

$$NaI(s) + Cl_2(g) \rightarrow NaCl(s) + I_2(l)$$

$\Delta S = -79.9$ J/mol•K

$\Delta G = -98.0$ kJ/mol

490. The element bromine can be produced by the reaction of hydrogen bromide and manganese(IV) oxide:

$$4HBr(g) + MnO_2(s) \rightarrow MnBr_2(s) + 2H_2O(l) + Br_2(l)$$

ΔH for the reaction is −291.3 kJ/mol at 25°C. Use this value and the following values of ΔH_f^0 to calculate ΔH_f^0 of $MnBr_2(s)$.

$\Delta H_{f_{HBr}}^0 = -36.29$ kJ/mol

$\Delta H_{f_{MnO_2}}^0 = -520.0$ kJ/mol

$\Delta H_{f_{H_2O}}^0 = -285.8$ kJ/mol

$\Delta H_{f_{Br_2}}^0 = 0.00$ kJ/mol

491. Calculate the change in entropy, ΔS, at 25°C for the reaction of calcium carbide with water to produce acetylene gas:

$$CaC_2(s) + 2H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$$

$\Delta G = -147.7$ kJ/mol

$\Delta H = -125.6$ kJ/mol

492. Calculate the free energy change for the explosive decomposition of ammonium nitrate at 25°C. Note that H_2O is a gas in this reaction:

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$$

$\Delta S = 446.4$ J/mol•K

493. In locations where natural gas, which is mostly methane, is not available, many people burn propane, which is delivered by truck and stored in a tank under pressure.

a. Write the chemical equations for the complete combustion of 1 mol of methane, CH_4, and 1 mol of propane, C_3H_8.

b. Calculate the enthalpy change for each reaction to determine the amount of heat evolved off by burning 1 mol of each fuel.

c. Using the molar heats of combustion you calculated, determine the heat output per kilogram of each fuel. Which fuel yields more heat per unit mass?

494. The hydration of acetylene to form acetaldehyde is shown in the following equation:

$$C_2H_2(g) + H_2O(l) \rightarrow CH_3CHO(l)$$

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Use heats of combustion for acetylene and acetaldehyde to compute the enthalpy of the above reaction.

$$C_2H_2(g) + 2O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$

$\Delta H = -1299.6$ kJ/mol

$$CH_3CHO(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

$\Delta H = -1166.9$ kJ/mol

495. Calculate the enthalpy for the combustion of decane. ΔH_f^0 for liquid decane is -300.9 kJ/mol.

$$C_{10}H_{22}(l) + 15O_2(g) \rightarrow 10CO_2(g) + 11H_2O(l)$$

496. Find the enthalpy of the reaction of magnesium oxide with hydrogen chloride:

$$MgO(s) + 2HCl(g) \rightarrow MgCl_2(s) + H_2O(l)$$

Use the following equations and data.

$$Mg(s) + 2HCl(g) \rightarrow MgCl_2(s) + H_2(g)$$

$\Delta H = -456.9$ kJ/mol

$$Mg(s) + O_2(g) \rightarrow MgO(s)$$

$\Delta H = -601.6$ kJ/mol

$$H_2O(l) \rightarrow H_2(g) + O_2(g)$$

$\Delta H = +285.8$ kJ/mol

497. What is the free energy change for the following reaction at 25°C?

$$2NaOH(s) + 2Na(s) \xrightarrow{\Delta} 2\,Na_2O(s) + H_2(g)$$

$\Delta S = 10.6$ J/mol•K

$\Delta H^0_{f_{NaOH}} = -425.9$ kJ/mol

498. The following equation represents the reaction between gaseous HCl and gaseous ammonia to form solid ammonium chloride:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Calculate the entropy change in J/mol•K for the reaction of hydrogen chloride and ammonia at 25°C using the following data and the table following item 500.

$\Delta G = -91.2$ kJ/mol

499. The production of steel from iron involves the removal of many impurities in the iron ore. The following equations show some of the purifying reactions. Calculate the enthalpy for each reaction. Use the table following item 500 and the data given.

a. $3C(s) + Fe_2O_3(s) \rightarrow 3CO(g) + 2Fe(s)$

$\Delta H^0_{f_{CO(g)}} = -110.53$ kJ/mol

b. $3Mn(s) + Fe_2O_3(s) \rightarrow 3MnO(s) + 2Fe(s)$

$\Delta H^0_{f_{MnO(s)}} = -384.9$ kJ/mol

c. $12P(s) + 10Fe_2O_3(s) \rightarrow 3P_4O_{10}(s) + 20Fe(s)$

$\Delta H^0_{f_{P_4O_{10}(s)}} = -3009.9$ kJ/mol

d. $3Si(s) + 2Fe_2O_3(s) \rightarrow 3SiO_2(s) + 4Fe(s)$

$\Delta H^0_{f_{SiO_2(s)}} = -910.9$ kJ/mol

e. $3S(s) + 2Fe_2O_3(s) \rightarrow 3SO_2(g) + 4Fe(s)$

Equilibrium, Section 18-1

500. Calculate the equilibrium constants for the following hypothetical reactions. Assume that all components of the reactions are gaseous.

a. $A \rightleftarrows C + D$

For problems 498–499

Substance	ΔH_f^0 (kj/mol)	Substance	ΔH_f^0 (kj/mol)
$NH_3(g)$	−45.9	$HF(g)$	−273.3
$NH_4Cl(s)$	−314.4	$H_2O(g)$	−241.82
$NH_4F(s)$	−125	$H_2O(l)$	−285.8
$NH_4NO_3(s)$	−365.56	$H_2O_2(l)$	−187.8
$Br_2(l)$	0.00	$H_2SO_4(l)$	−813.989
$CaCO_3(s)$	−1207.6	$FeO(s)$	−825.5
$CaO(s)$	−634.9	$Fe_2O_3(s)$	−1118.4
$CH_4(g)$	−74.9	$MnO_2(s)$	−520.0
$C_3H_8(g)$	−104.7	$N_2O(g)$	+82.1
$CO_2(g)$	−393.5	$O_2(g)$	0.00
$F_2(g)$	0.00	$Na_2O(s)$	−414.2
$H_2(g)$	0.00	$Na_2SO_3(s)$	−1101
$HBr(g)$	−36.29	$SO_2(g)$	−296.8
$HCl(g)$	−92.3	$SO_3(g)$	−395.7

At equilibrium, the concentration of A is 2.24×10^{-2} M and the concentrations of both C and D are 6.41×10^{-3} M.

b. $A + B \rightleftarrows C + D$

At equilibrium, the concentrations of both A and B are 3.23×10^{-5} M and the concentrations of both C and D are 1.27×10^{-2} M.

c. $A + B \rightleftarrows 2C$

At equilibrium, the concentrations of both A and B are 7.02×10^{-3} M and the concentration of C is 2.16×10^{-2} M.

d. $2A \rightleftarrows 2C + D$

At equilibrium, the concentration of A is 6.59×10^{-4} M. The concentration of C is 4.06×10^{-3} M, and the concentration of D is 2.03×10^{-3} M.

e. $A + B \rightleftarrows C + D + E$

At equilibrium, the concentrations of both A and B are 3.73×10^{-4} M and the concentrations of C, D, and E are 9.35×10^{-4} M.

f. $2A + B \rightleftarrows 2C$

At equilibrium, the concentration of A is 5.50×10^{-3} M, the concentration of B is 2.25×10^{-3}, and the concentration of C is 1.02×10^{-2} M.

501. Calculate the concentration of product D in the following hypothetical reaction:

$$2A(g) \rightleftarrows 2C(g) + D(g)$$

At equilibrium, the concentration of A is 1.88×10^{-1} M, the concentration of C is 6.56 M, and the equilibrium constant is 2.403×10^2.

502. At a temperature of 700 K, the equilibrium constant is 3.164×10^3 for the following reaction system for the hydrogenation of ethene, C_2H_4, to ethane, C_2H_6:

$$C_2H_4(g) + H_2(g) \rightleftarrows C_2H_6(g)$$

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What will be the equilibrium concentration of ethene if the concentration of H_2 is 0.0619 M and the concentration of C_2H_6 is 1.055 M?

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503. Using the reaction $A + 2B \rightleftarrows C + 2D$, determine the equilibrium constant if the following equilibrium concentrations are found. All components are gases.

[A] = 0.0567 M

[B] = 0.1171 M

[C] = 0.000 3378 M

[D] = 0.000 6756 M

504. In the reaction $2A \rightleftarrows 2C + 2D$, determine the equilibrium constant when the following equilibrium concentrations are found. All components are gases.

[A] = 0.1077 M

[C] = 0.000 4104 M

[D] = 0.000 4104 M

505. Calculate the equilibrium constant for the following reaction. Note the phases of the components.

$$2A(g) + B(s) \rightleftarrows C(g) + D(g)$$

The equilibrium concentrations of the components are

[A] = 0.0922 M

[C] = 4.11×10^{-4} M

[D] = 8.22×10^{-4} M

506. The equilibrium constant of the following reaction for the decomposition of phosgene at 25°C is 4.282×10^{-2}.

$$COCl_2(g) \rightleftarrows CO(g) + Cl_2(g)$$

a. What is the concentration of $COCl_2$ when the concentrations of both CO and Cl_2 are 5.90×10^{-3} M?

b. When the equilibrium concentration of $COCl_2$ is 0.003 70 M, what are the concentrations of CO and Cl_2? Assume the concentrations are equal.

507. Consider the following hypothetical reaction.

$$A(g) + B(s) \rightleftarrows C(g) + D(s)$$

a. If $K = 1$ for this reaction at 500 K, what can you say about the concentrations of A and C at equilibrium?

b. If raising the temperature of the reaction results in an equilibrium with a higher concentration of C than A, how will the value of K change?

508. The following reaction occurs when steam is passed over hot carbon. The mixture of gases it generates is called *water gas* and is useful as an industrial fuel and as a source of hydrogen for the production of ammonia.

$$C(s) + H_2O(g) \rightleftarrows CO(g) + H_2(g)$$

The equilibrium constant for this reaction is 4.251×10^{-2} at 800 K. If the equilibrium concentration of $H_2O(g)$ is 0.1990 M, what concentrations of CO and H_2 would you expect to find?

509. When nitrogen monoxide gas comes in contact with air, it oxidizes to the brown gas nitrogen dioxide according to the following equation:

$$2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$$

a. The equilibrium constant for this reaction at 500 K is 1.671×10^4. What concentration of NO_2 is present at equilibrium if $[NO] = 6.200 \times 10^{-2}$ M and $[O_2] = 8.305 \times 10^{-3}$ M?

b. At 1000 K, the equilibrium constant, K, for the same reaction is 1.315×10^{-2}. What will be the concentration of NO_2 at 1000 K given the same concentrations of NO and O_2 as were in (a)?

510. Consider the following hypothetical reaction, for which $K = 1$ at 300 K:

$$A(g) + B(g) \rightleftarrows 2C(g)$$

a. If the reaction begins with equal concentrations of A and B and a zero concentration of C, what can you say about the relative concentrations of the components at equilibrium?

b. Additional C is introduced at equilibrium, and the temperature remains constant. When equilibrium is restored, how will the concentrations of all components have changed? How will K have changed?

511. The equilibrium constant for the following reaction of hydrogen gas and bromine gas at 25°C is 5.628×10^{18}:

$$H_2(g) + Br_2(g) \rightleftarrows 2HBr(g)$$

a. Write the equilibrium expression for this reaction.

b. Assume that equimolar amounts of H_2 and Br_2 were present at the beginning. Calculate the equilibrium concentration of H_2 if the concentration of HBr is 0.500 M.

c. If equal amounts of H_2 and Br_2 react, which reaction component will be present in the greatest concentration at equilibrium? Explain your reasoning.

512. The following reaction reaches an equilibrium state:

$$N_2F_4(g) \rightleftarrows 2NF_2(g)$$

At equilibrium at 25°C the concentration of N_2F_4 is found to be 0.9989 M and the concentration of NF_2 is 1.131×10^{-3} M. Calculate the equilibrium constant of the reaction.

513. The equilibrium between dinitrogen tetroxide and nitrogen dioxide is represented by the following equation:

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

A student places a mixture of the two gases into a closed gas tube and allows the reaction to reach equilibrium at 25°C. At equilibrium, the concentration of N_2O_4 is found to be 5.95×10^{-1} M and the concentration of NO_2 is found to be 5.24×10^{-2} M. What is the equilibrium constant of the reaction?

514. Consider the following equilibrium system:

$$NaCN(s) + HCl(g) \rightleftarrows HCN(g) + NaCl(s)$$

a. Write a complete expression for the equilibrium constant of this system.

b. The equilibrium constant for this reaction is 2.405×10^6. What is the concentration of HCl remaining when the concentration of HCN is 0.8959 M?

515. The following reaction is used in the industrial production of hydrogen gas:

$$CH_4(g) + H_2O(g) \rightleftarrows CO(g) + 3H_2(g)$$

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The equilibrium constant of this reaction at 298 K (25°C) is 3.896×10^{-27}, but at 1100 K the constant is 3.112×10^{2}.

a. What do these equilibrium constants tell you about the progress of the reaction at the two temperatures?

b. Suppose the reaction mixture is sampled at 1100 K and found to contain 1.56 M of hydrogen, 3.70×10^{-2} M of methane, and 8.27×10^{-1} M of gaseous H_2O. What concentration of carbon monoxide would you expect to find?

516. Dinitrogen tetroxide, N_2O_4, is soluble in cyclohexane, a common nonpolar solvent. While in solution, N_2O_4 can break down into NO_2 according to the following equation:

$$N_2O_4(cyclohexane) \rightleftarrows NO_2(cyclohexane)$$

At 20°C, the following concentrations were observed for this equilibrium reaction:

$[N_2O_4] = 2.55 \times 10^{-3}$ M

$[NO_2] = 10.4 \times 10^{-3}$ M

What is the value of the equilibrium constant for this reaction? Note: the chemical equation must be balanced first.

517. The reaction given in item 516 also occurs when the dinitrogen tetroxide and nitrogen dioxide are dissolved in carbon tetrachloride, CCl_4, another nonpolar solvent.

$$N_2O_4(CCl_4) \rightleftarrows NO_2(CCl_4)$$

The following experimental data were obtained at 20°C:

$[N_2O_4] = 2.67 \times 10^{-3}$ M

$[NO_2] = 10.2 \times 10^{-3}$ M

Calculate the value of the equilibrium constant for this reaction occurring in carbon tetrachloride.

Equilibrium of Acids and Bases, K_a and K_b, Section 18-3

518. At 25°C, a 0.025 M solution of formic acid, HCOOH, is found to have a hydronium ion concentration of 2.03×10^{-3} M. Calculate the ionization constant of formic acid.

519. The pH of a 0.400 M solution of iodic acid, HIO_3, is 0.726 at 25°C. What is the K_a at this temperature?

520. The pH of a 0.150 M solution of hypochlorous acid, HClO, is found to be 4.55 at 25°C. Calculate the K_a for HClO at this temperature.

521. The compound propylamine, $CH_3CH_2CH_2NH_2$, is a weak base. At equilibrium, a 0.039 M solution of propylamine has an OH^- concentration of 3.74×10^{-3} M. Calculate the pH of this solution and K_b for propylamine.

522. The K_a of nitrous acid is 4.6×10^{-4} at 25°C. Calculate the $[H_3O^+]$ of a 0.0450 M nitrous acid solution.

Mixed Review

523. Hydrazoic acid, HN_3, is a weak acid. The $[H_3O^+]$ of a 0.102 M solution of hydrazoic acid is 1.39×10^{-3} M. Determine the pH of this solution, and calculate K_a at 25°C for HN_3.

524. Bromoacetic acid, $BrCH_2COOH$, is a moderately weak acid. A 0.200 M solution of bromoacetic acid has a H_3O^+ concentration of 0.0192 M. Determine the pH of this solution and the K_a of bromoacetic acid at 25°C.

525. A base, B, dissociates in water according to the following equation:

$$B + H_2O \rightleftarrows BH^+ + OH^-$$

Complete the following table for base solutions with the characteristics given.

Initial [B]	*[B] at Equilibrium*	*$[OH^-]$*	*K_b*	*$[H_3O^+]$*	*pH*
a. 0.400 M	NA	2.70×10^{-4} M	?	? M	?
b. 0.005 50 M	? M	8.45×10^{-4} M	?	NA	?
c. 0.0350 M	? M	? M	?	? M	11.29
d. ? M	0.006 28 M	0.000 92 M	?	NA	?

526. The solubility of benzoic acid, C_6H_5COOH, in water at 25°C is 2.9 g/L. The pH of this saturated solution is 2.92. Determine K_a at 25°C for benzoic acid. (Hint: first calculate the initial concentration of benzoic acid.)

527. A 0.006 50 M solution of ethanolamine, $H_2NCH_2CH_2OH$, has a pH of 10.64 at 25°C. Calculate the K_b of ethanolamine. What concentration of undissociated ethanolamine remains at equilibrium?

528. The weak acid hydrogen selenide, H_2Se, has two hydrogen atoms that can form hydronium ions. The second ionization is so small that the concentration of the resulting H_3O^+ is insignificant. If the $[H_3O^+]$ of a 0.060 M solution of H_2Se is 2.72×10^{-3} M at 25°C, what is the K_a of the first ionization?

529. Pyridine, C_5H_5N, is a very weak base. Its K_b at 25°C is 1.78×10^{-9}. Calculate the $[OH^-]$ and pH of a 0.140 M solution. Assume that the concentration of pyridine at equilibrium is equal to its initial concentration because so little pyridine is dissociated.

530. A solution of a monoprotic acid, HA, at equilibrium is found to have a 0.0208 M concentration of nonionized acid. The pH of the acid solution is 2.17. Calculate the initial acid concentration and K_a for this acid.

531. Pyruvic acid, $CH_3COCOOH$, is an important intermediate in the metabolism of carbohydrates in the cells of the body. A solution made by dissolving 438 mg of pyruvic acid in 10.00 mL of water is found to have a pH of 1.34 at 25°C. Calculate K_a for pyruvic acid.

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532. The $[H_3O^+]$ of a solution of acetoacetic acid, CH_3COCH_2COOH, is 4.38×10^{-3} M at 25°C. The concentration of nonionized acid is 0.0731 M at equilibrium. Calculate K_a for acetoacetic acid at 25°C.

533. The K_a of 2-chloropropanoic acid, $CH_3CHClCOOH$, is 1.48×10^{-3}. Calculate the $[H_3O^+]$ and the pH of a 0.116 M solution of 2-chloropropionic acid. Let $x = [H_3O^+]$. The degree of ionization of the acid is too large to ignore. If your set up is correct, you will have a quadratic equation to solve.

534. Sulfuric acid ionizes in two steps in water solution. For the first ionization shown in the following equation, the K_a is so large that in moderately dilute solution the ionization can be considered 100%.

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

The second ionization is fairly strong, and $K_a = 1.3 \times 10^{-2}$:

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^{2-}$$

Calculate the total $[H_3O^+]$ and pH of a 0.0788 M H_2SO_4 solution. Hint: If the first ionization is 100%, what will $[HSO_4^-]$ and $[H_3O^+]$ be? Remember to account for the already existing concentration of H_3O^+ in the second ionization. Let $x = [SO_4^{2-}]$.

535. The hydronium ion concentration of a 0.100 M solution of cyanic acid, HOCN, is found to be 5.74×10^{-3} M at 25°C. Calculate the ionization constant of cyanic acid. What is the pH of this solution?

536. A solution of hydrogen cyanide, HCN, has a 0.025 M concentration. The cyanide ion concentration is found to be 3.16×10^{-6} M.

a. What is the hydronium ion concentration of this solution?
b. What is the pH of this solution?
c. What is the concentration of nonionized HCN in the solution? Be sure to use the correct number of significant figures.
d. Calculate the ionization constant of HCN.
e. How would you characterize the strength of HCN as an acid?
f. Determine the $[H_3O^+]$ for a 0.085 M solution of HCN.

537. A 1.20 M solution of dichloroacetic acid, CCl_2HCOOH, at 25°C has a hydronium ion concentration of 0.182 M.

a. What is the pH of this solution?
b. What is the K_a of dichloroacetic acid at 25°C?
c. What is the concentration of nonionized dichloroacetic acid in this solution?
d. What can you say about the strength of dichloroacetic acid?

538. Phenol, C_6H_5OH, is a very weak acid. The pH of a 0.215 M solution of phenol at 25°C is found to be 5.61. Calculate the K_a for phenol.

539. A solution of the simplest amino acid, glycine (NH_2CH_2COOH), is prepared by dissolving 3.75 g in 250.0 mL of water at 25°C. The pH of this solution is found to be 0.890.

a. Calculate the molarity of the glycine solution.
b. Calculate the K_a for glycine.

540. Trimethylamine, $(CH_3)_3N$, dissociates in water the same way that NH_3 does—by accepting a proton from a water molecule. The $[OH^-]$ of a 0.0750 M solution of trimethylamine at 25°C is 2.32×10^{-3} M. Calculate the pH of this solution and the K_b of trimethylamine.

541. Dimethylamine, $(CH_3)_2NH$, is a weak base similar to the trimethylamine in item 540. A 5.00×10^{-3} M solution of dimethylamine has a pH of 11.20 at 25°C. Calculate the K_b of dimethylamine. Compare this K_b with the K_b for trimethylamine that you calculated in item 540. Which substance is the stronger base?

542. Hydrazine dissociates in water solution according to the following equations:

$$H_2NNH_2 + H_2O(l) \rightleftarrows H_2NNH_3^+(aq) + OH^-(aq)$$
$$H_2NNH_3^+(aq) + H_2O(l) \rightleftarrows H_3NNH_3^{2+}(aq) + OH^-(aq)$$

The K_b of this second dissociation is 8.9×10^{-16}, so it contributes almost no hydroxide ions in solution and can be ignored here.

a. The pH of a 0.120 M solution of hydrazine at 25°C is 10.50. Calculate K_b for the first ionization of hydrazine. Assume that the original concentration of H_2NNH_2 does not change.
b. Make the same assumption as you did in (a) and calculate the $[OH^-]$ of a 0.020 M solution.
c. Calculate the pH of the solution in (b).

Equilibrium of Salts, K_{sp}, Section 18-4

543. Silver bromate, $AgBrO_3$, is slightly soluble in water. A saturated solution is found to contain 0.276 g $AgBrO_3$ dissolved in 150.0 mL of water. Calculate K_{sp} for silver bromate.

544. 2.50 L of a saturated solution of calcium fluoride leaves a residue of 0.0427 g of CaF_2 when evaporated to dryness. Calculate the K_{sp} of CaF_2.

545. The K_{sp} of calcium sulfate, $CaSO_4$, is 9.1×10^{-6}. What is the molar concentration of $CaSO_4$ in a saturated solution?

546. A salt has the formula X_2Y, and its K_{sp} is 4.25×10^{-7}.

a. What is the molarity of a saturated solution of the salt?
b. What is the molarity of a solution of AZ if its K_{sp} is the same value?

In each of the following problems, include the calculated ion product with your answer.

547. Will a precipitate of $Ca(OH)_2$ form when 320. mL of a 0.046 M solution of NaOH mixes with 400. mL of a 0.085 M $CaCl_2$ solution? K_{sp} of $Ca(OH)_2$ is 5.5×10^{-6}.

548. 20.00 mL of a 0.077 M solution of silver nitrate, $AgNO_3$, is mixed with 30.00 mL of a 0.043 M solution of sodium acetate, $NaC_2H_3O_2$. Does a precipitate form? The K_{sp} of $AgC_2H_3O_2$ is 2.5×10^{-3}.

549. If you mix 100. mL of 0.036 M $Pb(C_2H_3O_2)_2$ with 50. mL of 0.074 M NaCl, will a precipitate of $PbCl_2$ form? The K_{sp} of $PbCl_2$ is 1.9×10^{-4}.

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550. If 20.00 mL of a 0.0090 M solution of $(NH_4)_2S$ is mixed with 120.00 mL of a 0.0082 M solution of $Al(NO_3)_3$, does a precipitate form? The K_{sp} of Al_2S_3 is 2.00×10^{-7}.

Mixed Review

551. The molar concentration of a saturated calcium chromate, $CaCrO_4$, solution is 0.010 M at 25°C. What is the K_{sp} of calcium chromate?

552. A 10.00 mL sample of a saturated lead selenate solution is found to contain 0.00136 g of dissolved $PbSeO_4$ at 25°C. Determine the K_{sp} of lead selenate.

553. A 22.50 mL sample of a saturated copper(I) thiocyanate, CuSCN, solution at 25°C is found to have a 4.0×10^{-6} M concentration.
- **a.** Determine the K_{sp} of CuSCN.
- **b.** What mass of CuSCN would be dissolved in 1.0×10^3 L of solution?

554. A saturated solution of silver dichromate, $Ag_2Cr_2O_7$, has a concentration of 3.684×10^{-3} M. Calculate the K_{sp} of silver dichromate.

555. The K_{sp} of barium sulfite, $BaSO_3$, at 25°C is 8.0×10^{-7}.
- **a.** What is the molar concentration of a saturated solution of $BaSO_3$?
- **b.** What mass of $BaSO_3$ would dissolve in 500. mL of water?

556. The K_{sp} of lead(II) chloride at 25°C is 1.9×10^{-4}. What is the molar concentration of a saturated solution at 25°C?

557. The K_{sp} of barium carbonate at 25°C is 1.2×10^{-8}.
- **a.** What is the molar concentration of a saturated solution of $BaCO_3$ at 25°C?
- **b.** What volume of water would be needed to dissolve 0.10 g of barium carbonate?

558. The K_{sp} of $SrSO_4$ is 3.2×10^{-7} at 25°C.
- **a.** What is the molar concentration of a saturated $SrSO_4$ solution?
- **b.** If 20.0 L of a saturated solution of $SrSO_4$ were evaporated to dryness, what mass of $SrSO_4$ would remain?

559. The K_{sp} of strontium sulfite, $SrSO_3$, is 4.0×10^{-8} at 25°C. If 1.0000 g of $SrSO_3$ is stirred in 5.0 L of water until the solution is saturated and then filtered, what mass of $SrSO_3$ would remain?

560. The K_{sp} of manganese(II) arsenate is 1.9×10^{-11} at 25°C. What is the molar concentration of $Mn_3(AsO_4)_2$ in a saturated solution? Note that five ions are produced from the dissociation of $Mn_3(AsO_4)_2$.

561. Suppose that 30.0 mL of a 0.0050 M solution of $Sr(NO_3)_2$ is mixed with 20.0 mL of a 0.010 M solution of K_2SO_4 at 25°C. The K_{sp} of $SrSO_4$ is 3.2×10^{-7}.
- **a.** What is the ion product of the ions that can potentially form a precipitate?
- **b.** Does a precipitate form?

562. Lead(II) bromide, $PbBr_2$, is slightly soluble in water. Its K_{sp} is 6.3×10^{-6} at 25°C. Suppose that 120. mL of a 0.0035 M solution of $MgBr_2$ is mixed with 180. mL of a 0.0024 M $Pb(C_2H_3O_2)_2$ solution at 25°C.
- **a.** What is the ion product of Br^- and Pb^{2+} in the mixed solution?
- **b.** Does a precipitate form?

563. The K_{sp} of $Mg(OH)_2$ at 25°C is 1.5×10^{-11}.
- **a.** Write the equilibrium equation for the dissociation of $Mg(OH)_2$.
- **b.** What volume of water would be required to dissolve 0.10 g of $Mg(OH)_2$?
- **c.** Considering that magnesium hydroxide is essentially insoluble, why is it possible to titrate a suspension of $Mg(OH)_2$ to an equivalence point with a strong acid such as HCl?

564. Lithium carbonate is somewhat soluble in water; its K_{sp} at 25°C is 2.51×10^{-2}.
- **a.** What is the molar concentration of a saturated Li_2CO_3 solution?
- **b.** What mass of Li_2CO_3 would you dissolve in order to make 3440 mL of saturated solution?

565. A 50.00 mL sample of a saturated solution of barium hydroxide, $Ba(OH)_2$, is titrated to the equivalence point by 31.61 mL of a 0.3417 M solution of HCl. Determine the K_{sp} of $Ba(OH)_2$.

566. Calculate the K_{sp} for salts represented by QR that dissociate into two ions, Q^+ and R^-, in each of the following solutions:
- **a.** saturated solution of QR is 1.0 M
- **b.** saturated solution of QR is 0.50 M
- **c.** saturated solution of QR is 0.1 M
- **d.** saturated solution of QR is 0.001 M

567. Suppose that salts QR, X_2Y, KL_2, A_3Z, and D_2E_3 form saturated solutions that are 0.02 M in concentration. Calculate K_{sp} for each of these salts.

568. The K_{sp} at 25°C of silver bromide is 5.0×10^{-13}. What is the molar concentration of a saturated AgBr solution? What mass of silver bromide would dissolve in 10.0 L of saturated solution at 25°C?

569. The K_{sp} at 25°C for calcium hydroxide is 5.5×10^{-6}.
- **a.** Calculate the molarity of a saturated $Ca(OH)_2$ solution.
- **b.** What is the OH^- concentration of this solution?
- **c.** What is the pH of the saturated solution?

570. The K_{sp} of magnesium carbonate is 3.5×10^{-8} at 25°C. What mass of $MgCO_3$ would dissolve in 4.00 L of water at 25°C?

Redox Equations, Section 19-2

Reactions in Acidic Solution

Balance the following redox equations. Assume that all reactions take place in an acid environment where H^+ and H_2O are readily available.

571. $Fe + SnCl_4 \rightarrow FeCl_3 + SnCl_2$

572. $H_2O_2 + FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O$

573. $CuS + HNO_3 \rightarrow Cu(NO_3)_2 + NO + S + H_2O$

574. $K_2Cr_2O_7 + HI \rightarrow CrI_3 + KI + I_2 + H_2O$

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Reactions in Basic Solution

Balance the following redox equations. Assume that all reactions take place in a basic environment where OH^- and H_2O are readily available.

575. $CO_2 + NH_2OH \rightarrow CO + N_2 + H_2O$

576. $Bi(OH)_3 + K_2SnO_2 \rightarrow Bi + K_2SnO_3$

(Both of the potassium-tin-oxygen compounds dissociate into potassium ions and tin-oxygen ions.)

Mixed Review

Balance each of the following redox equations. Unless stated otherwise, assume that the reaction occurs in acidic solution.

577. $Mg + N_2 \rightarrow Mg_3N_2$

578. $SO_2 + Br_2 + H_2O \rightarrow HBr + H_2SO_4$

579. $H_2S + Cl_2 \rightarrow S + HCl$

580. $PbO_2 + HBr \rightarrow PbBr_2 + Br_2 + H_2O$

581. $S + HNO_3 \rightarrow NO_2 + H_2SO_4 + H_2O$

582. $NaIO_3 + N_2H_4 + HCl \rightarrow N_2 + NaICl_2 + H_2O$ (N_2H_4 is hydrazine; do not separate it into ions.)

583. $MnO_2 + H_2O_2 + HCl \rightarrow MnCl_2 + O_2 + H_2O$

584. $AsH_3 + NaClO_3 \rightarrow H_3AsO_4 + NaCl$ (AsH_3 is arsine, the arsenic analogue of ammonia, NH_3.)

585. $K_2Cr_2O_7 + H_2C_2O_4 + HCl \rightarrow CrCl_3 + CO_2 + KCl + H_2O$ ($H_2C_2O_4$ is oxalic acid; it can be treated as $2H^+ + C_2O_4^{2-}$.)

586. $Hg(NO_3)_2 \xrightarrow{heat} HgO + NO_2 + O_2$ (The reaction is not in solution.)

587. $HAuCl_4 + N_2H_4 \rightarrow Au + N_2 + HCl$ ($HAuCl_4$ can be considered as $H^+ + AuCl_4^-$.)

588. $Sb_2(SO_4)_3 + KMnO_4 + H_2O \rightarrow H_3SbO_4 + K_2SO_4 + MnSO_4 + H_2SO_4$

589. $Mn(NO_3)_2 + NaBiO_3 + HNO_3 \rightarrow Bi(NO_3)_2 + HMnO_4 + NaNO_3 + H_2O$

590. $H_3AsO_4 + Zn + HCl \rightarrow AsH_3 + ZnCl_2 + H_2O$

591. $KClO_3 + HCl \rightarrow Cl_2 + H_2O + KCl$

592. The same reactants as in item 591 can combine in the following way when more $KClO_3$ is present. Balance the equation.

$$KClO_3 + HCl \rightarrow Cl_2 + ClO_2 + H_2O + KCl$$

593. $MnCl_3 + H_2O \rightarrow MnCl_2 + MnO_2 + HCl$

594. $NaOH + H_2O + Al \rightarrow NaAl(OH)_4 + H_2$ in basic solution

595. $Br_2 + Ca(OH)_2 \rightarrow CaBr_2 + Ca(BrO_3)_2 + H_2O$ in basic solution

596. $N_2O + NaClO + NaOH \rightarrow NaCl + NaNO_2 + H_2O$ in basic solution

597. Balance the following reaction, which can be used to prepare bromine in the laboratory:

$$HBr + MnO_2 \rightarrow MnBr_2 + H_2O + Br_2$$

598. The following reaction occurs when gold is dissolved in *aqua regia*. Balance the equation.

$$Au + HCl + HNO_3 \rightarrow HAuCl_4 + NO + H_2O$$

Electrochemistry, Section 19-4

Use the reduction potentials in the table on page 955 to determine whether the following reactions are spontaneous as written. Report the E^0_{cell} for the reactions.

599. $Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$

600. $Pb^{2+} + Fe^{2+} \rightarrow Fe^{3+} + Pb$

601. $Mn^{2+} + 4H_2O + Sn^{2+} \rightarrow MnO_4^- + 8H^+ + Sn$

602. $MnO_4^{2-} + Cl_2 \rightarrow MnO_4^- + 2Cl^-$

603. $Hg_2^{2+} + 2MnO_4^{2-} \rightarrow 2Hg + 2MnO_4^-$

604. $2Li^+ + Pb \rightarrow 2Li + Pb^{2+}$

605. $Br_2 + 2Cl^- \rightarrow 2Br^- + Cl_2$

606. $S + 2I^- \rightarrow S^{2-} + I_2$

If a cell is constructed in which the following pairs of reactions are possible, what would be the cathode reaction, the anode reaction, and the overall cell voltage?

607. $Ca^{2+} + 2e^- \rightleftarrows Ca$
$Fe^{3+} + 3e^- \rightleftarrows Fe$

608. $Ag^+ + e^- \rightleftarrows Ag$
$S + 2H^+ + 2e^- \rightleftarrows H_2S$

609. $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$
$Sn^{2+} + 2e^- \rightleftarrows Sn$

610. $Cu^{2+} + 2e^- \rightleftarrows Cu$
$Au^{3+} + 3e^- \rightleftarrows Au$

Mixed Review

Use reduction potentials to determine whether the reactions in the following 10 problems are spontaneous.

611. $Ba + Sn^{2+} \rightarrow Ba^{2+} + Sn$

612. $Ni + Hg^{2+} \rightarrow Ni^{2+} + Hg$

613. $2Cr^{3+} + 7\,H_2O + 6Fe^{3+} \rightarrow Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+}$

614. $Cl_2 + Sn \rightarrow 2Cl^- + Sn^{2+}$

615. $Al + 3Ag^+ \rightarrow Al^{3+} + 3Ag$

616. $Hg_2^{2+} + S^{2-} \rightarrow 2Hg + S$

617. $Ba + 2Ag^+ \rightarrow Ba^{2+} + 2Ag$

618. $2I^- + Ca^{2+} \rightarrow I_2 + Ca$

619. $Zn + 2MnO_4^- \rightarrow Zn^{2+} + 2MnO_4^{2-}$

620. $2Cr^{3+} + 3Mg^{2+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 3Mg$

In the following problems, you are given a pair of reduction half-reactions. If a cell were constructed in which the pairs of half-reactions were possible,

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what would be the balanced equation for the overall cell reaction that would occur? Write the half-reactions that occur at the cathode and anode, and calculate the cell voltage.

621. $Cl_2 + 2e^- \rightleftarrows 2Cl^-$
$Ni^{2+} + 2e^- \rightleftarrows Ni$

622. $Fe^{3+} + 3e^- \rightleftarrows Fe$
$Hg^{2+} + 2e^- \rightleftarrows Hg$

623. $MnO_4^- + e^- \rightleftarrows MnO_4^{2-}$
$Al^{3+} + 3e^- \rightleftarrows Al$

624. $MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$
$S + 2H^+ + 2e^- \rightleftarrows H_2S$

625. $Ca^{2+} + 2e^- \rightleftarrows Ca$
$Li^+ + e^- \rightleftarrows Li$

626. $Br_2 + 2e^- \rightleftarrows 2Br^-$
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$

627. $Sn^{2+} + 2e^- \rightleftarrows Sn$
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$

628. $Zn^{2+} + 2e^- \rightleftarrows Zn$
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O$

629. $Ba^{2+} + 2e^- \rightleftarrows Ba$
$Ca^{2+} + 2e^- \rightleftarrows Ca$

630. $Hg_2^{2+} + 2e^- \rightleftarrows 2Hg$
$Cd^{2+} + 2e^- \rightleftarrows Cd$

For problems 599–606

Reduction Half-reaction	*Standard Electrode Potential, E^0 (in volts)*	*Reduction Half-reaction*	*Standard Electrode Potential, E^0 (in volts)*
$MnO_4^- + 8H^+ + 5e^- \rightleftarrows Mn^{2+} + 4H_2O$	+1.50	$Fe^{3+} + 3e^- \rightleftarrows Fe$	−0.04
$Au^{3+} + 3e^- \rightleftarrows Au$	+1.50	$Pb^{2+} + 2e^- \rightleftarrows Pb$	−0.13
$Cl_2 + 2e^- \rightleftarrows 2Cl^-$	+1.36	$Sn^{2+} + 2e^- \rightleftarrows Sn$	−0.14
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftarrows 2Cr^{3+} + 7H_2O$	+1.23	$Ni^{2+} + 2e^- \rightleftarrows Ni$	−0.26
$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$	+1.22	$Cd^{2+} + 2e^- \rightleftarrows Cd$	−0.40
$Br_2 + 2e^- \rightleftarrows 2Br^-$	+1.07	$Fe^{2+} + 2e^- \rightleftarrows Fe$	−0.45
$Hg^{2+} + 2e^- \rightleftarrows Hg$	+0.85	$S + 2e^- \rightleftarrows S^{2-}$	−0.48
$Ag^+ + e^- \rightleftarrows Ag$	+0.80	$Zn^{2+} + 2e^- \rightleftarrows Zn$	−0.76
$Hg_2^{2+} + 2e^- \rightleftarrows 2Hg$	+0.80	$Al^{3+} + 3e^- \rightleftarrows Al$	−1.66
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.77	$Mg^{2+} + 2e^- \rightleftarrows Mg$	−2.37
$MnO_4^- + e^- \rightleftarrows MnO_4^{2-}$	+0.56	$Na^+ + e^- \rightleftarrows Na$	−2.71
$I_2 + 2e^- \rightleftarrows 2I^-$	+0.54	$Ca^{2+} + 2e^- \rightleftarrows Ca$	−2.87
$Cu^{2+} + 2e^- \rightleftarrows Cu$	+0.34	$Ba^{2+} + 2e^- \rightleftarrows Ba$	−2.91
$S + 2H^+(aq) + 2e^- \rightleftarrows H_2S(aq)$	+0.14	$K^+ + e^- \rightleftarrows K$	−2.93
$2H^+(aq) + 2e^- \rightleftarrows H_2$	0.00	$Li^+ + e^- \rightleftarrows Li$	−3.04

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